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CATALYZED BIO-OXIDATION AND TERTIARY TREATMENT OF INTEGRATED TEXTILE WASTEWATERS

Alvin J. Snyder, et al

Cone Mills Corporation

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16. Abstract

This report describes the observations from preliminary studies and pilot plant operations that were initiated to upgrade the waste effluent of an integrated textile dye mill. The biological pilot plant was designed to utilize activated carbon on the basis that the presence of carbon enhances bio-degradation.

To meet the proposed water standards, tertiary treatment of the effluent was also necessary. Two methods of attaining better water effluent were investigated. A conventional method, the addition of an alum system, with alum recovery was added to the biological treatment system. Although the effluent quality improved, trace color remained in the supernatant. An adsorbent resin system was tested and found effective in upgrading the waste effluent to recreational standards.

The results of preliminary studies and the pilot plant indicate that carbon catalysis enhances biological degradation, and satisfactory tertiary treatment can be achieved with an alum and resin system.

17a. Descriptors: *Water Pollution, *Pollution Abatement, *Textile Wastewater treatment, Wastewater Re-use, Upgrading Biological treatment.

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EPA-660/2-74-039
June 1974

CATALYZED BIO-OXIDATION AND TERTIARY TREATMENT OF INTEGRATED TEXTILE WASTEWATERS

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The results of preliminary studies and the pilot plant indicate that carbon catalysis enhances biological degradation, and satisfactory tertiary treatment can be achieved with an alum and resin system.

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SECTION I

CONCLUSIONS

Over a twelve month period, beginning in September 1971, a study was made of the methods by which an existing secondary waste treatment plant for an integrated textile mill could be upgraded to meet more stringent water standards.

Based on the results of the study conducted at the Cone Mills Corporation, Greensboro, North Carolina facility, the following conclusions have been reached:

1. The presence of carbon in aerated biological reactors enhances the rates of biological degradation of color bodies and organic substrates as experienced in the textile wet processing operations.

2. Alum treatment of biologically treated effluent reduces the total organic carbon content and color by about one-third, but alum concentrations of 300 - 400 milligrams per liter are required.

3. Alum regeneration is possible by acidification of alum sludge with sulfuric acid to a pH of 2.0.

4. Alum regeneration is necessary to make the process economically feasible.

5. Ten percent make-up alum is required to offset losses in the alum recovery system.

6. Color removal is reduced when the pH of the alum system falls below 5.0.

7. Adsorbent resins are effective in removing dissolved residual organic color bodies.

8. Regeneration of adsorbent resin is effectively accomplished by elution with warm caustic solution and the eluate can be acceptably disposed of via recycling.

9. Resin treatment can be effective as a tertiary treatment method either before or after an alum treatment system.

10. Regular sludge wasting is necessary for good color removal and reduces heavy metals concentration in the sludge.

11. No reductions in ammonia nitrogen were observed because of the solubility of the ammonium compounds.

12. High levels of chlorine significantly reduce the color of the alum treated waste.

13. The estimated capital cost for a 3,785 cubic meter per day plant is $854,500 for the biological system; for the alum system $304,500; and for the resin system $236,500. The total installed cost including contingencies, land and contractor fees is $1,490,000.

14. The operating expenses based on chemical costs, utilities, and labor for the plant would be $0.28 per 3.79 cubic meters waste treated.

SECTION II

RECOMMENDATIONS

1. As a result of the laboratory studies and pilot plant operations, efforts should proceed toward a full-scale demonstration of a carbon catalyzed system with stage aeration.

2. In general, the presence of carbon in a biological system enhances biological degradation, and the addition of carbon to an existing aeration basin (lagoon) should be evaluated as a method of increasing effluent quality.

3. A carbon catalyzed system with stage aeration appears to treat biodegradable wastes efficiently, and the effectiveness on municipal wastes should be investigated.

4. A full-scale carbon catalyzed system should be demonstrated with alum and resin systems for tertiary treatment of textile dyeing wastes.

SECTION III

INTRODUCTION

Cone Mills Corporation, located in Greensboro, North Carolina (see Figure 1), is a manufacturer of finished textile fabrics. The combined wastewater discharged into the North Buffalo Creek is generated from several sources: 1) an integrated denim mill; 2) an integrated flannel and other flat goods mill; and 3) a printing and finishing mill. The treatment for the dyes and finishing chemicals in the Cone Mills' effluent was found to be insufficient to meet the new proposed North Carolina State water quality standards.

The amount of wastewater from the Cone Mills' treatment plant varies from 11,355 to 13,626 cubic meters per day (m^3/day). The wastewater content fluctuates according to the type of process and dye used. A successful waste treatment program had to consider several types of processes as well as a variety of dyes. The average wastewater characteristics, the anticipated effluent characteristics after treatment, and the effluent standards desired by the North Carolina Department of Water and Air Resources are presented in Table 1.

Cone Mills had an existing on-site secondary waste treatment plant, which discharged to the nearby North Buffalo Creek. The wastewater was handled within this existing system in the following manner:

> The waste first entered aerobic holding ponds with a combined detention time of 48 hours. The wastewater was biologically degraded in this step by mixing with 10% domestic sewage for seeding purposes, and fed into a 24 hour detention aeration basin. This basin operated at a suspended solids (SS) level of 12,000 - 14,000 milligrams per liter (mg/l). The waste was settled for four hours in clarifiers and the sludge was recycled to the aeration basin. Aeration and mixing were provided by mechanical aerators. Waste sludge was handled under contract by the Greensboro Municipal System with a maximum allowable waste volume of 114 m^3/day. The clarifier effluent received further clarification in a newly built (Spring, 1971) lagoon with a five to seven day detention time. The liquid effluent was chlorinated, reaerated for 45 minutes for saturation, and then discharged into the creek.

In the past, this level of treatment had been sufficient for creek discharges; however, Buffalo Creek will soon become one of the water sources of a reservoir formed by the Jordan Dam across the Haw River. The resultant proposed water quality standards for Cone Mills' discharge require 99% five day biochemical oxygen demand (BOD_5) reduction,

Figure 1

Location Map
Cone Mills Corporation
Greensboro, North Carolina

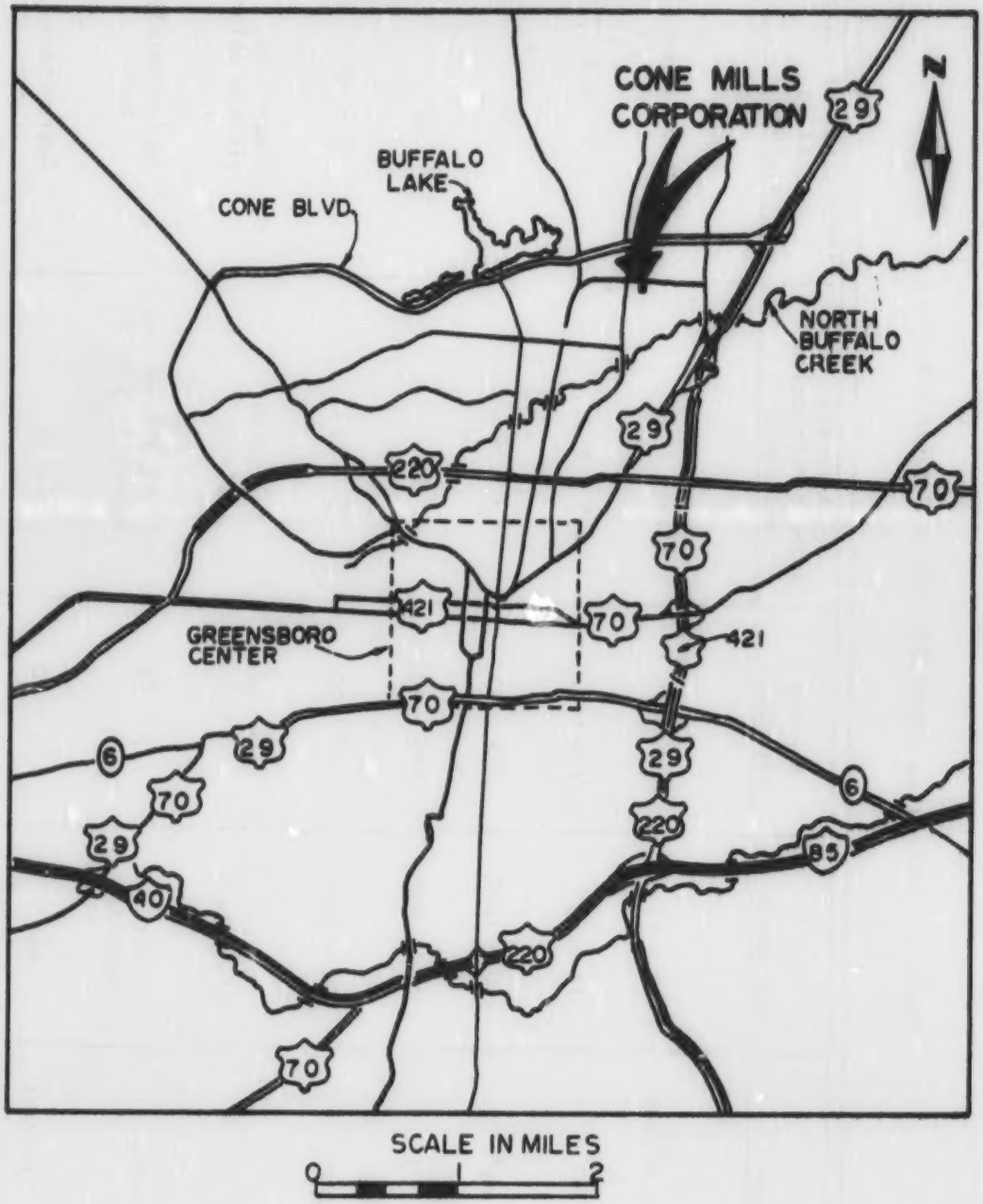


Table 1. CONE MILLS' TREATMENT EFFLUENT CHARACTERISTICS

Parameter	Raw waste	Present secondary	New tertiary under construction estimated	North Carolina state desired standards
Volume, m^3/day	11.4 - 15.1	11.4 - 15.1	11.4 - 15.1	Not specified
pH	12 - 13	7.5 - 8.0	7.5 - 8.0	7.5 - 8.0
BOD_5, mg/l	600 - 1000	25 - 85	10 - 50	5
COD, mg/l	1200 - 2000	200 - 300	200	30
SS, mg/l	100 - 200	20 - 50	5 - 20	0 - 10
Color	Varied blue/black	Light green to yellow	Yellowish - green	Clear - no visible color
Phosphate, mg/l	Not recorded	5 - 10	Slightly lower avg. but still 5 - 10	Approximately zero
Total Kjeldahl Nitrogen, mg/l	Not recorded	5 - 10	5 - 10	Approximately zero

a 99+% phosphate reduction, a 99+% Kjeldahl nitrogen reduction, a 98% chemical oxygen demand (COD) reduction, a 96% suspended solids reduction, and virtually 100% color removal (see Table 1). The same problem of upgrading the performance of the existing Cone Mills' treatment plant to meet these high discharge quality standards within possible economic bounds will be facing many other large textile producers.

BIO-CATALYSIS THEORY

The large surface area of activated carbon, as much as 1,000 square meter/gram, and the chemical functionality of the available surface are the major factors responsible for activated carbon's adsorptive action. This surface area is made up of micropores having diameters in the order of 10 - 1,000 Angstrom units. A combination of the action of Van der Waal's force of attraction and some chemical reactivity on the large surface area is responsible for the adsorbent properties of carbon.

Because of the relatively large size of bacterial cells (greater than 5,000 Angstrom units), a mechanism involving migration of bacteria into the carbon interstitial spaces is improbable. Bacteria do, however, have the ability to produce enzymes which function outside their cellular boundaries. The exo-enxymes are produced within the cell and then excreted by the organism to the surrounding media. Exo-enzymes function independently of the bacteria that produced them and are mainly digestive or hydrolytic in nature.

Exo-enzymes, being much smaller than a bacterial cell probably in the order of 10 Angstrom units, could easily diffuse into and out of the microporous structure. It is reasonable to assume that an enzyme-substrate relationship is possible within the carbon structure, i.e., a specific enzymatic substrate can be formed.

The carbon adsorption of the substrates and diffused enzyme interaction would act to provide a higher concentration of reactants, and thus allow a greater degree of intermolecular contact. It can be speculated that this higher concentration would result in an increased rate of degradation by the enzyme; hence, carbon would be behaving as a catalyst to biodegradation.

BIOLOGICAL REACTOR THEORY

The utilization of smaller multi-staged aerated lagoons rather than a large single basin results in a more efficient biological system capable of producing a higher quality effluent. The biokinetics of aerated activated sludge systems confirmed the observations.

Biological degradation of organic material is achieved by the process known as biological oxidation. In this process under aerated conditions, the organic material, or substrate, is broken down by enzymatic action to a form that can be utilized by the organism for cellular metabolism. The end products are carbon dioxide, water, new biological organisms and inert cellular material.

The rate of biological degradation for first order reactions is directly proportional to the concentration of the substrate at a given concentration of biological organisms[1] as shown in the relation below:

$$\frac{dS}{dt} \propto S \qquad (1)$$

where: S = substrate concentration

t = time

In general, it is apparent that for a given concentration of biological organisms, higher rates of removal may be achieved using higher substrate concentrations. Therefore, a biological waste treatment system capable of increasing the concentration of substrate by its physical design within the aerated basin is capable of degrading more substrate per unit basin volume.

RESIN ADSORPTION THEORY

Biological and chemical treatment of organic wastes often result in an effluent that has only trace amounts of color (less than 50 platinum-cobalt color units), yet the nature of the color may not meet aesthetic water quality standards. As a result, treatment after biological and chemical treatment may be necessary. Treatment by means of adsorbent resins removes residual color to a level invisible to the naked eye.

Adsorbent resins are composed of hard, insoluble, polymeric particles that possess a high surface area and porosity. Various compounds in solution, including organic materials, are attracted to the resin surface by the action of Van der Waal's forces. A weak bond is formed between the resin structure and the adsorbed compound which can be broken by adverse chemical conditions such as high pH.

The introduction of caustic to the adsorbent-adsorbate complex results in severance of the bond and the release of the adsorbate to the caustic solution.

Such a process is applicable to the removal from solution of trace color. The color body is readily adsorbed by the resin, rendering a colorfree solution. When the resin has adsorbed its capacity of color bodies, it is regenerated by the addition of caustic solution. The resultant colored caustic regenerate solution is of relatively small volume (1%) and is treated in the biological lagoons for eventual color degradation.

CHEMICAL PRECIPITATION AND COAGULATION THEORY

Soluble organic materials can generally be removed from wastewater by a carbon catalyzed system. However, certain inorganic materials are not biologically degradable. Phosphates are a prime example. Thus, a further step in a waste treatment system becomes necessary to achieve high levels of effluent quality.

Chemical treatment of biologically degraded effluent will remove soluble and colloidal contaminants such as phosphates and an unsettled biological mass. This treatment process acts in two ways. First, the addition of chemicals such as alum causes some normally soluble materials such as phosphates to precipitate from solution due to the formation of insoluble chemical compounds. Secondly, the resultant suspended solids along with other colloidal particles are removed via chemical coagulation/precipitation.

Chemical coagulation of colloids and suspended solids is achieved by two processes: 1) the agglomeration of colloidal particles that are held in suspension by electrostatic forces; and 2) the chemical formation of large solid masses that capture suspended solids and cause them to settle out of solution. Coagulating agents (e.g., alum and ferric chloride) provide the charged ions that neutralize the electrostatically charged colloids. The agglomerated colloidal particles along with large suspended particles are captured by heavy aluminum and ferric hydroxides and rapidly settle out of solution.

PROJECT OBJECTIVES

The project was designed to evaluate approaches that would enable Cone Mills to meet the proposed water quality standards dictated by the construction of the Jordan Dam on the upper Haw River. A literature search and laboratory study were the basis of the preliminary work done to achieve these goals. On-site pilot plant scale studies were evaluated for their technical and economical feasibility.

The first recommendation involved the use of a surface active agent (activated carbon) added to a typical activated sludge biological system to catalyze biodegradation, thus requiring shorter detention times in the aeration basins.

The use of a coagulant such as alum for removing phosphates and reducing the color and organic content of the biologically treated waste effluent is a standard approach. The regeneration of the coagulant (not a standard approach) was another aspect in reducing operating costs and in reducing the volume of waste sludge for disposal.

A residual yellowish-green detectable coloration of the treated effluent persisted after carbon catalyzed biological treatment and alum flocculation and coagulation. Hence, to achieve an essentially colorless effluent, synthetic resin adsorbents were investigated as polishing agents after biological treatment alone, and after biological plus alum treatment.

SECTION IV

PRELIMINARY STUDIES

Preliminary studies were conducted in three areas:

Carbon Catalysis
Floc Studies & Alum Regeneration
Alum Selection

These investigatory phases were the basis for the selection of a commercial carbon for use in the pilot plant; the most efficient coagulant for removing phosphates and reducing color at Cone Mills; and the type of resin to be used to treat the effluent from the biological clarifier of the catalyzed biological system. Data collected also indicated the amount of sulphuric acid necessary for the alum regeneration as well as being the foundation for comparative analysis of the effectiveness of different resins tested.

CARBON CATALYSIS

The prospect of using a carbon catalyzed biological system was investigated on two separate occasions (June 3, 1970 and April - May, 1972) in a series of tests with Cone Mills' plant waste. In 1970, Cone Mills sent Fram Corporation two 55-gallon drum samples of the raw effluent (before biological treatment) and two 55-gallon drum samples of the final clarifier effluent (after biological treatment) for analysis.

Each waste was biologically degraded in a continuous aeration batch reactor with and without carbon. The concentration of granular carbon was 40 grams per 3000 milliliters (ml) of waste. After six days' aeration, the degraded waste was replaced with fresh waste and aeration continued. The supernatant, total oxygen demand (TOD), and color were measured at various intervals. TOD was chosen as an index at this point because it represents a close relationship to BOD_5, and it can be determined in five minutes as compared to five days for BOD_5.

Using a variable grating spectrophotometer, the light absorbance is measured at three wavelelengths - 350,450, and 550 millimicrons. If the light absorbance is greater than the instrument scale, the sample is diluted and a dilution multiplier is used to calculate the absorbance. The Fram color unit (FCU) is the sum of the corrected light absorbance at these three wavelengths. Although not correlative from sample to sample, the platinum-cobalt color units are in the magnitude of 1,000 times that of the Fram color unit.

The biological treatment of the raw influent from the non-catalyzed reactors yielded an equilibrium TOD concentration nearly equal to the final clarifier effluent of the same system, suggesting that a certain portion of the waste is difficult to degrade biologically. The presence of carbon, however, allowed nearly complete degradation of the organics (see Figures 2 and 3).

Specifically, the raw effluent in the non-catalyzed reactor reached an equilibrium TOD value representing 69% reduction in 48 hours. The color concentration dropped 49% in a period of 72 hours. The carbon catalyzed reactor experienced TOD and color reductions of 90% in the same time periods. This represents an additional 21% TOD and 41% color removal due to the presence of carbon. Figures 2 and 3 indicate the changes in TOD and color concentrations with respect to elapsed time. In all cases, the presence of carbon in the biological reactor greatly enhanced the removal of contaminants by effecting an increased kinetic rate of organic removal. The final equilibrium TOD and color concentrations were also much lower than the non-carbon counterparts.

The beneficial effect of carbon on biological systems was further confirmed in an on-site laboratory investigation in April and May of 1972 by Cone Mills' personnel. The carbon evaluation was conducted with four 3.78 liter containers. Two of these containers contained 20 grams of carbon. The others were used as control units and contained no carbon. One set made up of a container with carbon and a container without carbon was vigorously aerated. Another similar set of two more containers was moderately aerated. The filtered reactor effluent was measured each day to determine the effect of carbon. Fresh raw waste was added daily to each reactor.

After six test days, the aerated reactors experiencing the highest aerations were discontinued because of comparably high reactor colors. The moderately aerated reactors revealed that carbon definitely improved the biological degradation of the color bodies present in the raw waste (see Figure 4). Throughout the seven week test period, the reactor containing carbon gave consistently lower effluent colors. The reactor with carbon gave an average color of 0.173 Fram color unit, while the control reactor without carbon yielded a much higher color of 0.296 Fram color unit.

SELECTION OF CARBON

Selection of carbon to be utilized in the pilot studies depended largely on two factors. First, the carbon particle size had to be large enough so that the carbon would not be lost in the reactor effluent and yet provide a reasonable amount of surface area. Second, since commercial grades of carbon vary in their adsorbent capacity, a carbon with a high efficiency in TOD reduction and color removal had to be determined.

Figure 2

Effects of carbon on biodegradation
batch Aeration
(Nuchar WV-G carbon)
Waste of June 3, 1970

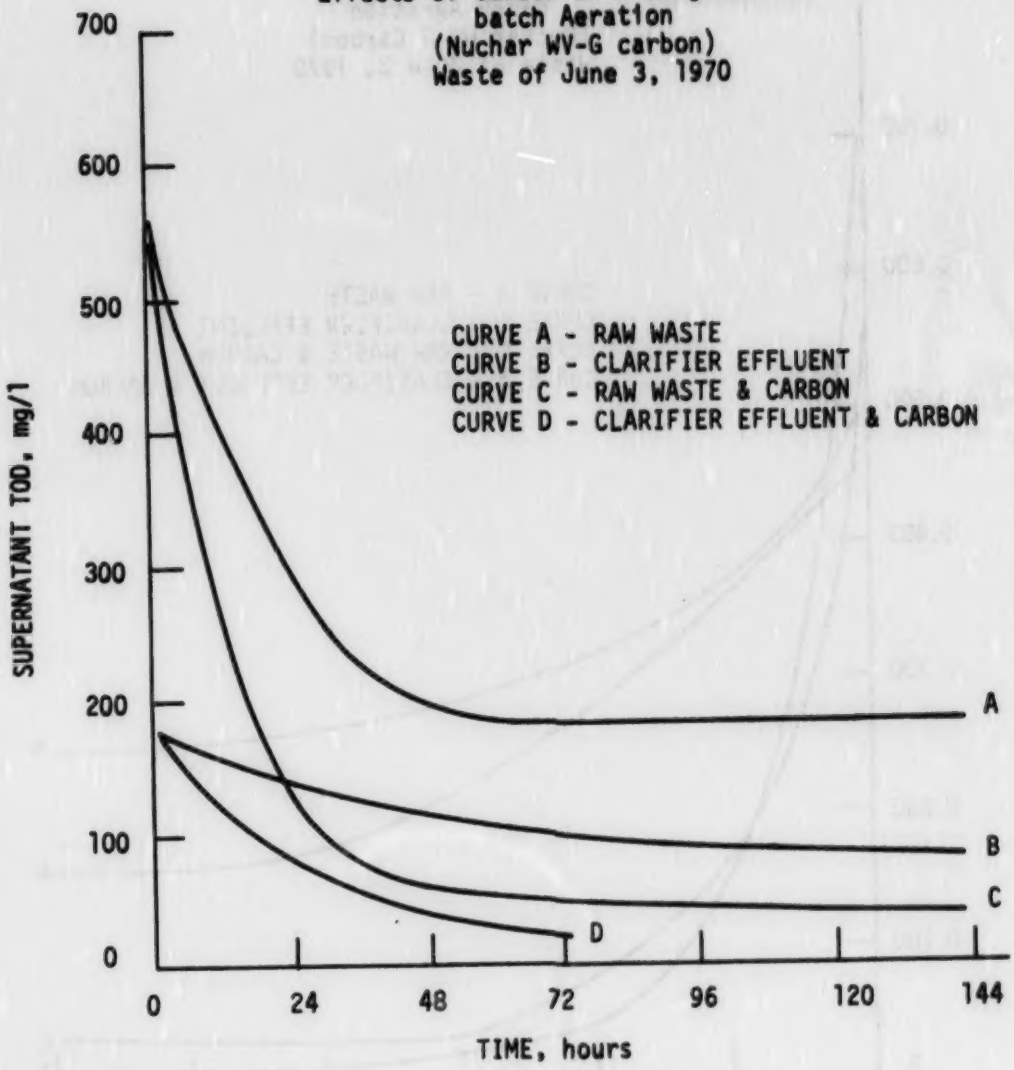


Figure 3

Effects of Carbon on Biodegradation
batch Aeration
(Nuchar WV-G Carbon)
Waste of June 3, 1970

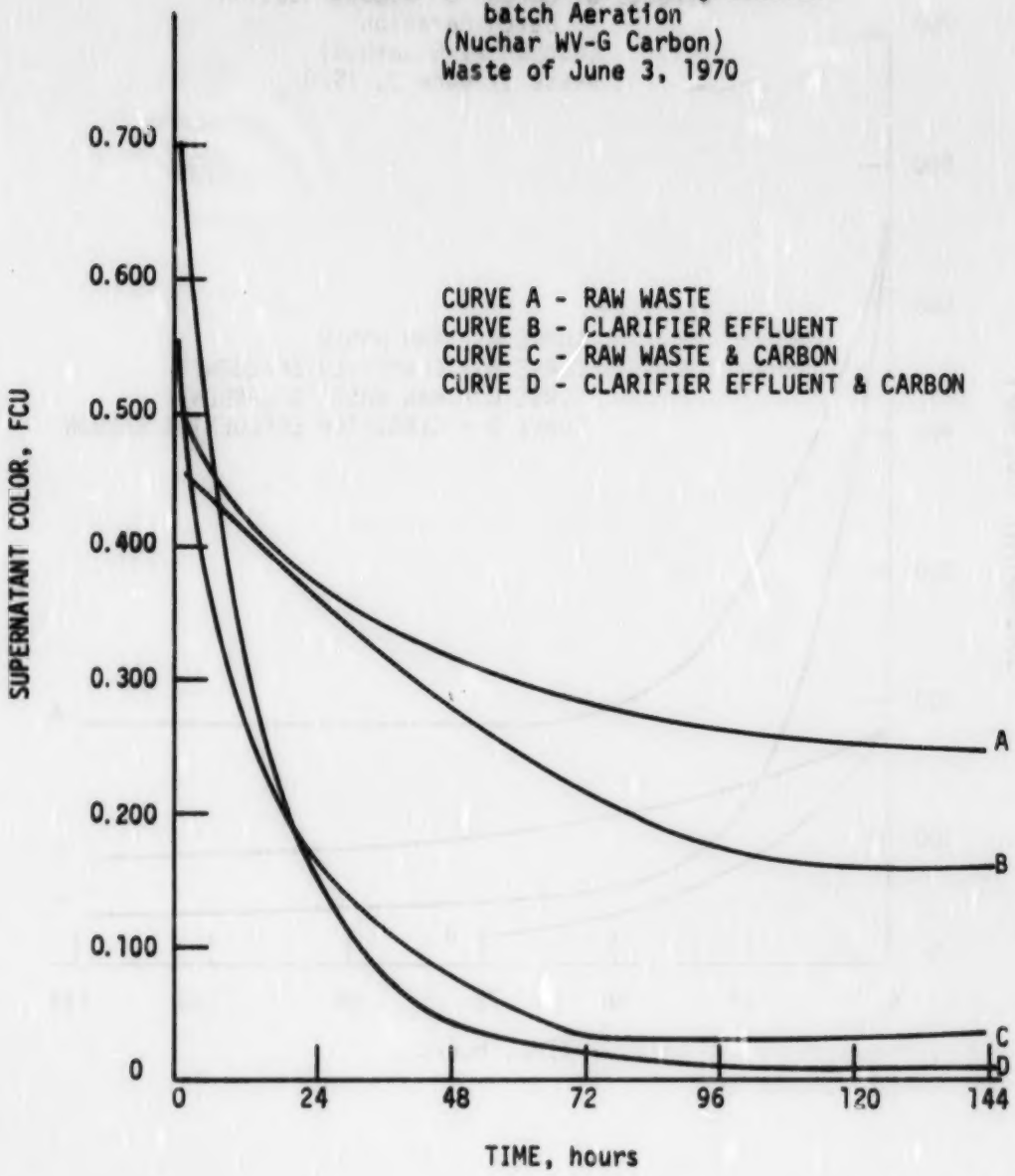
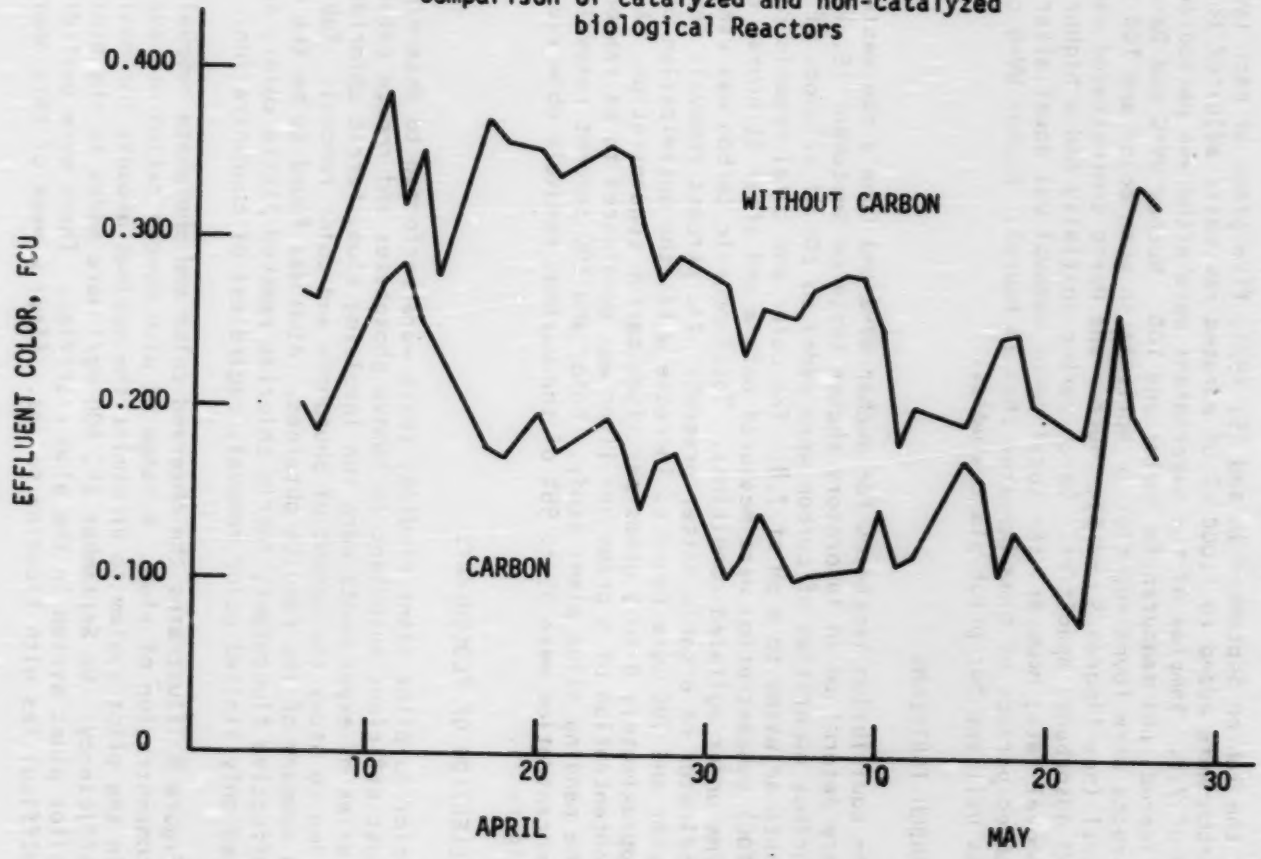


Figure 4

Comparison of catalyzed and non-catalyzed biological Reactors



A carbon of 12 x 40 mesh satisfied the parameters of the first condition. Several tests were performed to determine the efficiency of Nuchar WV-G, Darco, and Norit II in TOD reduction and color removal to meet the parameters of the second condition.

In the lab on September 14 and 15, 1971, five grams of each type of carbon were added to 1,000 ml of aerated raw waste adjusted to a pH of 7.8. Samples of the supernatant were withdrawn periodically, filtered, and measured for color and TOD. Nuchar WV-G and Darco carbons were found superior to Norit II in both color and TOD removal (see Figures 5 and 6). Nuchar and Darco demonstrated equal TOD adsorbent capacities. Darco carbon initially had a higher color removal rate; however, the total color removal was equal after extended periods of time (greater than 24 hours). Nuchar WV-G carbon was utilized for pilot plant studies.

CARBON ISOTHERMS

The equilibrium isotherms for Nuchar WV-G and Cone's raw waste were determined in laboratory shaker tests on September 15, 1971. Various quantities of carbon were added to 200 ml aliquots of raw waste adjusted to a pH of 7.8. The color and total organic carbon (TOC) concentration were measured before and after 65 hours' contact time under agitated conditions. Total organic carbon was used as an indicator of organic matter present. The percent removals for both color and TOC were found to increase until the optimization of approximately 8 to 9 grams per liter carbon concentration. A carbon concentration of 5 grams per liter was considered to be reasonable for the pending pilot plant study. Color and TOC percent removals at this concentration were 95 to 98% of the maximum removals observed (see Figure 7).

SELECTION OF FLOCCULANTS

Prior to pilot plant studies, tests were performed to determine the most efficient coagulant to remove phosphates and reduce color. A series of experiments were run involving alum, ferric chloride and lime to study the extent of phosphate and color removal. Table 2 is a summary of the results obtained. Alum was found to be the most effective flocculant, ferric chloride removed little color, and lime had only limited color removal, regardless of concentration.

Figure 8 illustrates the observed color and phosphate removal versus concentration of alum. A range of alum concentration was evaluated in the pilot system to determine the optimum amounts for maximum efficiency. On September 24, 400 mg/l were added to the biological pilot plant system in the alum clarifier. There were periodic difficulties with floating solids. After a week of this operation,

Figure 5

Adsorption rates of TOD on various carbons
Cone Mills' Effluent

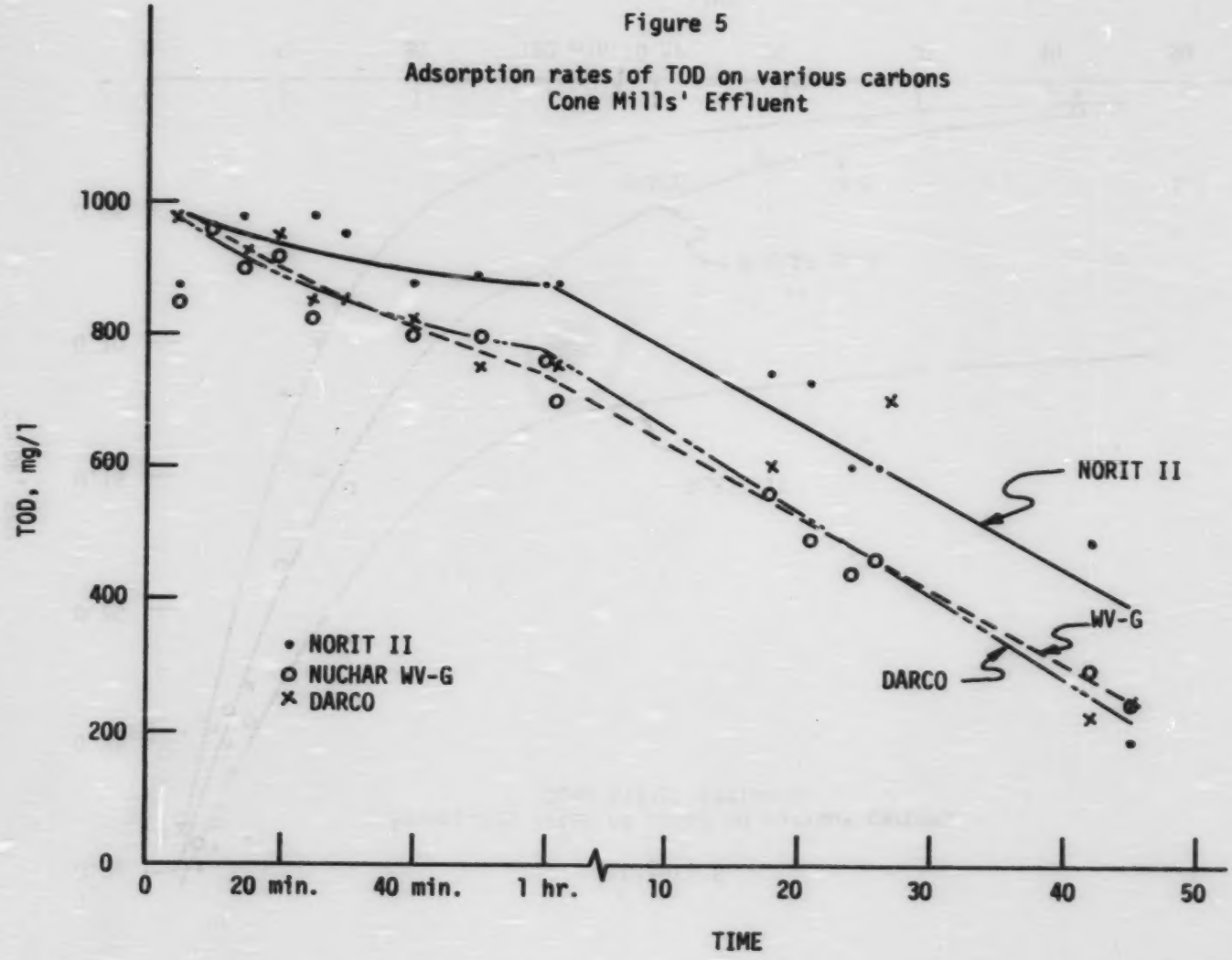


Figure 6

Adsorption rates of color on various carbons
Cone Mills' Effluent

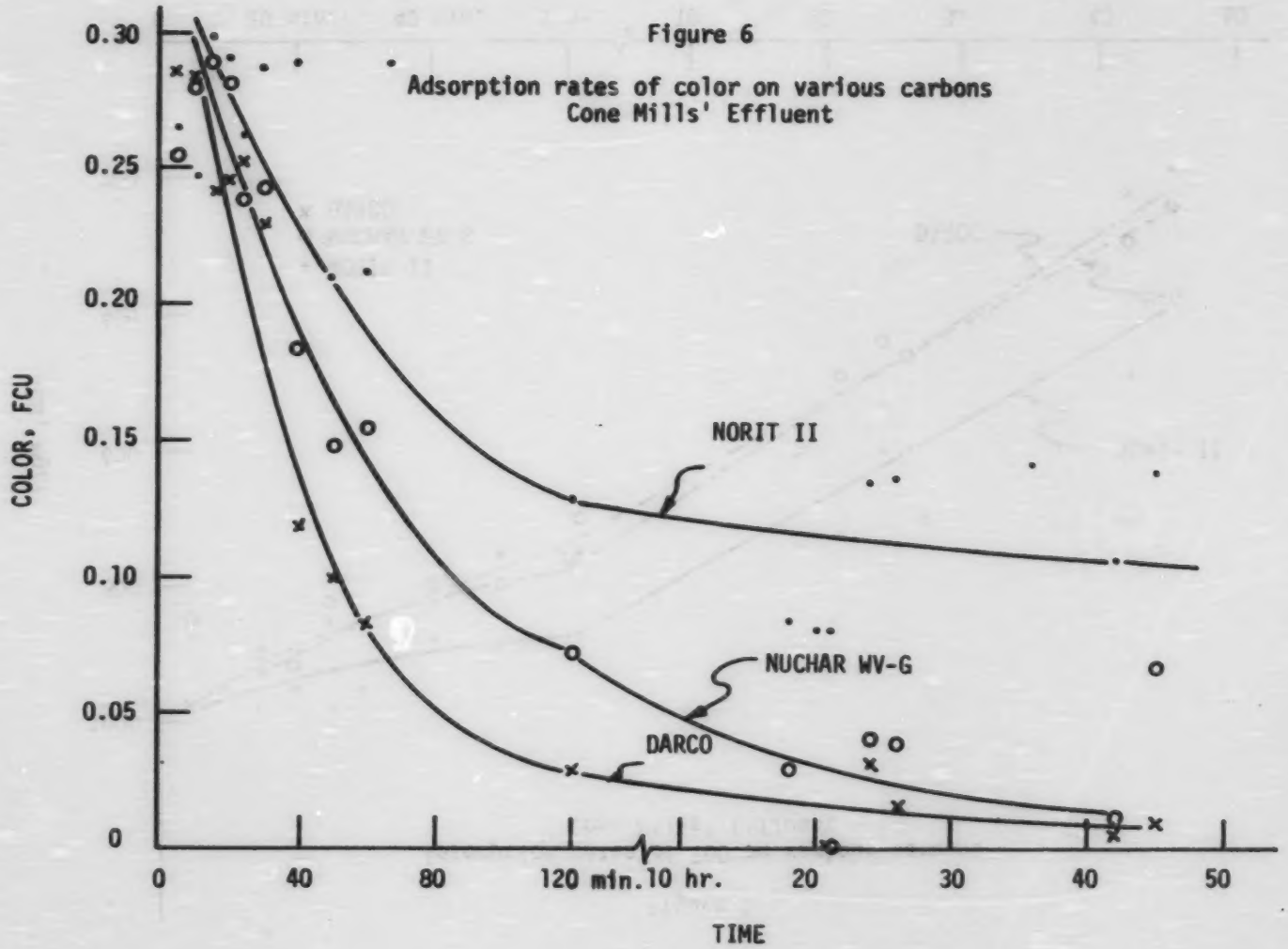


Table 2. CHEMICAL FLOCCULATION - LABORATORY STUDY

Treatment	pH[a]	Ortho-phosphate[b]	% Color removal[c]	COD[d]
Alum				
Untreated	6.6	0	0	0
100 mg/l	6.6	13	6	0
200 mg/l	6.2	18	20	4
300 mg/l	6.0	59	53	16
400 mg/l	5.6	100	85	26
500 mg/l	5.6	100	93	28
Ferric Chloride				
Untreated	8.0	0	0	0
100 mg/l	8.3	1	0	4
200 mg/l	7.9	10	0	6
300 mg/l	7.5	27	0	9
400 mg/l	6.5	82	0	24
500 mg/l	6.2	100	72	38
Lime				
Untreated	11.2	0	0	0
100 mg/l	11.5	56	33	4
200 mg/l	11.6	69	49	4
300 mg/l	11.6	73	49	6
400 mg/l	11.7	83	47	4
500 mg/l	11.8	-	49	6

[a] Initial pH = 7.8
[b] Initial concentration = 5.5 mg/l
[c] Initial color = 0.75 FCU, all samples analyzed after filtration with 1.2 micron membrane
[d] Initial concentration = 935 mg/l, all samples analyzed after filtration with 1.2 micron membrane

Figure 7

Color and TOC
equilibrium isotherms
Nuchar WV-G

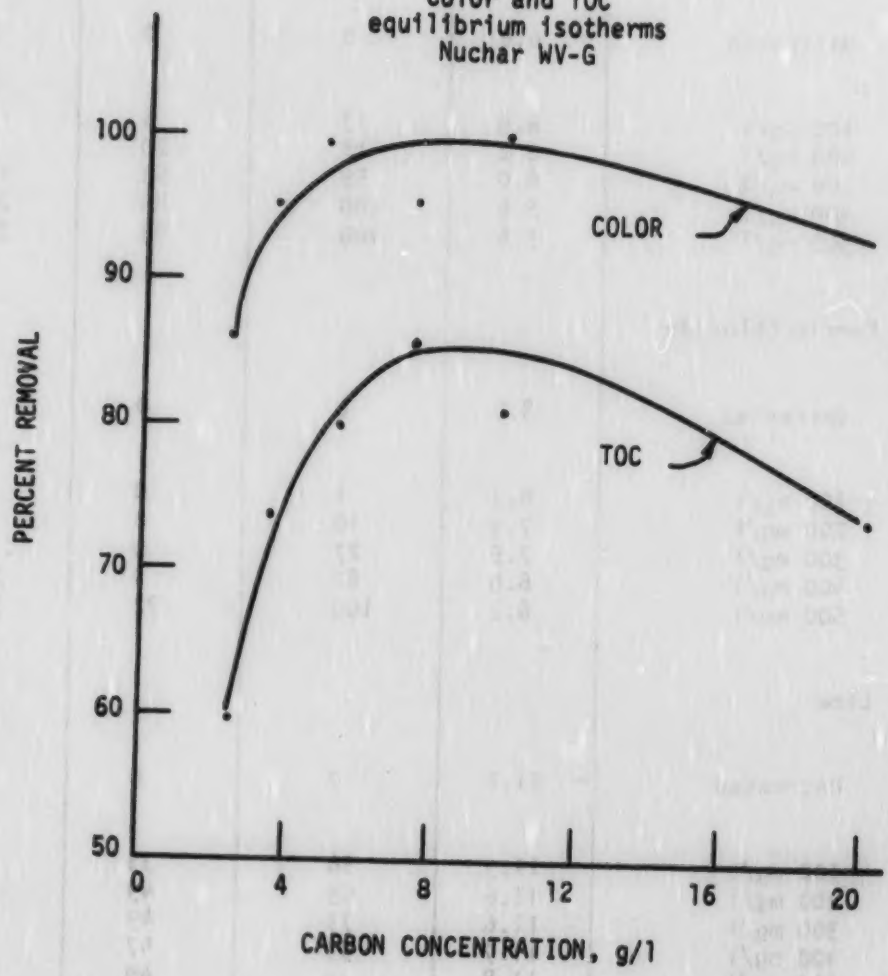
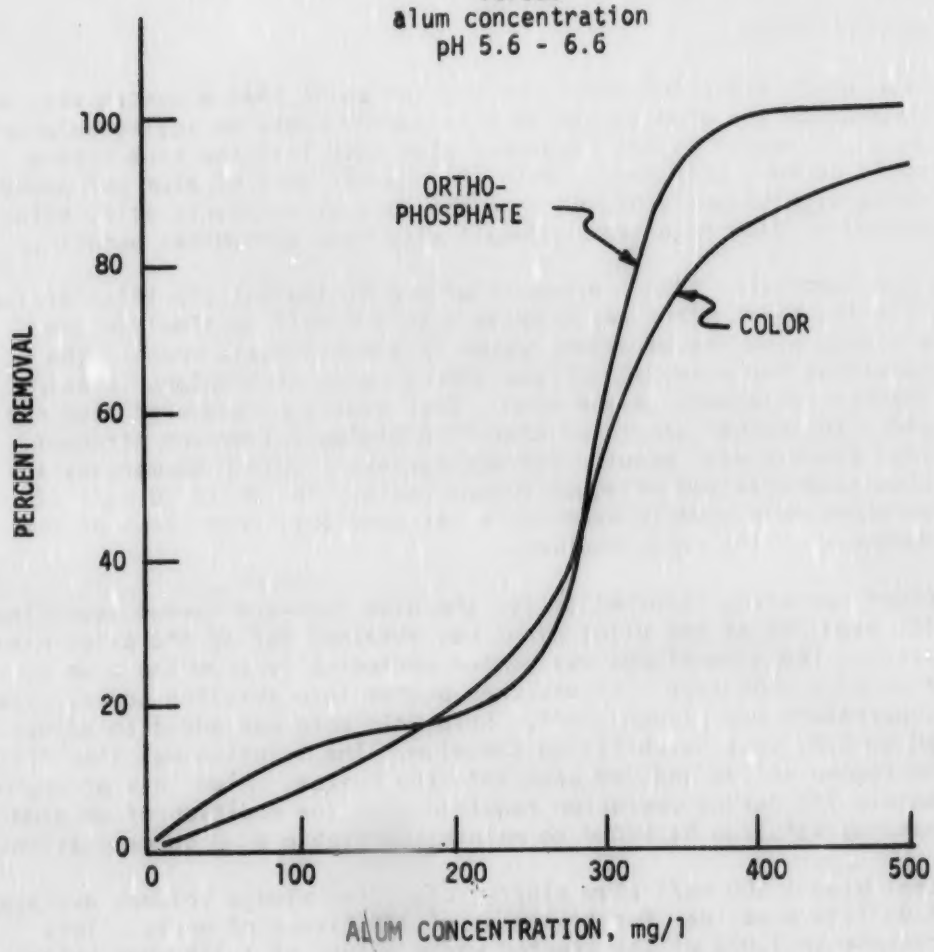


Figure 8

Phosphate and color removal
versus
alum concentration
pH 5.6 - 6.6



the alum was mixed with the clarified biological system effluent in a separate tank before being sent to an alum clarifier. This reduced but did not eliminate the problem of occasional floating solids.

On October 15, 1971, the alum concentration was reduced to 250 mg/l. Table 3 shows the TOC and color reductions produced by the alum system. This system consistently produces an effluent with less than one mg/l orthophosphates, and reduces the TOC and color by about one-third.

After the analysis of the effluent from the alum precipitation system with 250 mg/l, it was recommended that the alum concentration be raised to 300 mg/l in mid-January and continued at that level until the completion of the pilot plant studies.

ALUM RECOVERY

Laboratory and pilot plant testing indicated that a system that would regenerate the alum sludge to a dissolved state by adding sulphuric acid and recycling the recovered alum back into the alum system would be more efficient. With the present cost of alum per pound being significantly higher than the cost of sulphuric acid, this method of alum regeneration would also have economical benefits.

In a laboratory study, a sample of the biological clarifier effluent from the pilot plant was treated with 500 mg/l to simulate the proposed alum regeneration system in a bench scale model. The resultant hydroxide sludge was then treated with sulphuric acid (H_2SO_4) to regenerate the alum. The resulting recovered alum was added to another sample of clarified biological system effluent. This process was repeated for six cycles. Table 4 summarizes the alum recovered for an equal volume basis. The 40 to 50 mg/l of unrecoverable alum in each cycle was constant, regardless of the dosage with the range studied.

Other operating information for the alum recovery system (see Figure 12, page 34) at the pilot plant was obtained during the pilot plant study. The alum sludge was pumped periodically from the alum clarifier to a container. It was then poured into settling cones. The supernatant was siphoned off. Sulphuric acid was added to adjust the pH to 2.0, thus solubilizing the alum. The solution was then filtered to remove solids and fed back into the system. Alum loss of approximately 10% during operation required that the addition of an alum make-up solution be added to maintain a stable alum concentration.

Employing a 300 mg/l alum slurry, clarifier sludge volumes averaged 3.03 liters per day for treatment of 288 liters of waste. This represents 1.04% of the treated waste volume of 1.38% when extrapolated for a 400 mg/l alum slurry treatment. The recovered alum concentration was calculated to be 2.4% based upon a 50 mg/l alum-in-

Table 3. ALUM PRECIPITATION SYSTEM
Alum dosage = 250 mg/l

Date	Phosphate, mg/l		TOC, mg/l		Color, FCU	
	In	Out	In	Out	In	Out
11/2/71	4.2	0.5	70	45	0.065	0.025
11/3/71	3.9	0.6	65	70	0.150	0.100
11/4/71	2.8	0.8	70	45	0.140	0.090
11/5/71	0.9	0.7	85	40	0.160	0.115
11/9/71	0.4	0.1	45	40	0.200	0.100
11/10/71	0	0.1	120	80	0.215	0.185
11/11/71	0.2	0	85	55	0.230	0.190
11/12/71	0.1	0	95	70	0.215	0.185
Average	1.6	0.4	79	56	0.172	0.124

Table 4. ALUM REGENERATION LOSSES - LABORATORY STUDY
Alum dosage = 500 mg/l, Initial color = 0.219 FCU

	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
mg/l alum recovered	460	410	380	320	200	140
% alum recovered	92	89	93	84	63	70
mg/l alum lost[a]	40	50	30	60	120[b]	60
effluent color, FCU	0.117	0.088	0.125	0.062	0.084	0.133

[a] Average loss/cycle = 48 mg/l
[b] Statistically eliminated by Chauvenet's criterion[2]

sludge effluent loss. Hence, acid requirements for reclaiming the alum were found to be 50 ml of sulphuric acid (98% H_2SO_4) per 3.8 liters sludge, or 1.3% by volume.

Average suspended solids analyses of the influent waste and the alum clarifier effluent showed a 5 mg/l volatile solids decrease, and a 7 mg/l total suspended solids increase. The 12 mg/l solids addition was due to hydroxide floc carryover to the effluent, corresponding to a 46 mg/l alum loss in the clarifier. Also, the solubility of aluminum hydroxide in water is 1.04 mg/l, or an equivalent of 4 mg/l alum. Thus, the total permanent alum loss for the pilot plant operations was approximately 50 mg/l, agreeing well with the laboratory findings.

Alum regeneration by sulphuric acid addition to alum sludge was introduced to the pilot plants early in November, 1971. Except for a 1-1/2 month period starting in January, 1972, alum regeneration continued until the completion of the project.

pH

Another series of tests were performed to determine the pH effects on alum precipitation. Table 5 indicates that color reduction is fairly constant and that alum becomes insoluble from a pH of 5.0 through 7.5. At a pH of 4.5, color reduction decreases and the alum becomes more soluble.

RESIN SELECTION

Initially, a preliminary program was established to select the most efficient resins for use in extended studies. During January and February, 1972, three different adsorbent resins were tested on a pilot plant scale for their color removal capabilities. The resin pilot plant was set up to treat the effluent from the biological clarifier of the catalyzed biological pilot plant.

During the first period, three resins (Fram FR-37, FR-42, and FR-56) were tested for their relative color removal capabilities. FR-37 is a highly porous resin specifically designed to remove "organics" from water. FR-42 and FR-56 are macroreticular weakly basic anion exchange resins. FR-42 resin was tested throughout this period for use as a comparison to the performances of FR-37 and FR-56. Wide fluctuations in the resin performances were attributed to the unstability in the biological pilot plant at that time. Also fluctuations were inherent to the resin treatment process because of its cyclic nature; color removal decreased as the cycle neared completion. Regeneration and the start of a new cycle renewed the color removal efficiency.

Table 5. pH EFFECT ON ALUM PRECIPITATION
Alum dosage = 1,000 mg/l

pH	Effluent color[a]	mg/l alum in supernatant
7.5	0.079	10
7.0	0.082	10
6.8	0.081	10
6.5	0.060	10
6.0	0.067	10
5.5	0.068	10
5.0	0.066	10
4.5	0.118	120

[a] Influent color - 0.200 FCU

The daily percent color removals for FR-42 resin are shown in Figure 9. Color removals climbed to a peak of over 50% in late January, but quickly dropped to approximately 20% in early February. This sudden drop of resin efficiency corresponds to a dramatic decrease in color reductions in the biological pilot plant (see Figure 14, page 38). The percent color removals for FR-37 and FR-56 resins again reflected the instability present in the biological pilot plant (see Figure 14). Wide fluctuations are evident.

Two resins were compared to the FR-42 resin. During the nine day testing period for the FR-37 resin, color removals for the FR-37 and FR-42 were 30 and 44%, respectively. Therefore, FR-37 was considered less effective. The second resin, FR-56, to be tested with FR-42 was tested for a 14-day period. Color removal for the FR-42 was 26% and for the FR-56 - 30%. Therefore, FR-56 resin was selected for use in future extended pilot studies because of its superior color removal characteristics.

SEQUENCE OF RESIN TREATMENT

The resin treatment was considered both as a potential alternative to the alum pilot plant system and as an addition to the biological and alum treatment systems. Theoretically, it seemed that the resin system would be most effective following an alum flocculation system. The biologically and alum treated waste would be relatively free of suspended solids and thus resin fouling would be avoided. An additional consideration was that the resin system would experience smaller color loadings due to the partial color removal afforded by the alum flocculation system. The pilot plant operations provided the data for the studies conducted on the resin with biologically treated effluent. Laboratory tests on resin performance using biologically and alum treated effluent were conducted.

LABORATORY TEST PROCEDURE

FR-42 resin was selected for use in the laboratory test. A burette containing 50 ml of resin was used to treat the biologically clarified effluent after it had been flocculated with 400 mg/l alum. The waste was passed through the resin column at a flow rate that allowed a fifteen minute detention time. Twenty thousand ml of alum treated waste with approximately 0.10 FCU were fed through the burette before the color removal decreased to 50%. The resin demonstrated excellent color reductions as shown by its breakthrough curve in Figure 10.

The performance of FR-56 resin with biologically treated waste was compared to the FR-42 resin with alum treated, biologically treated effluent. Both types of resin were virgin resins at the beginning of the test periods. During the six-day period, FR-56 resin was

Figure 9

Resin pilot plant performance

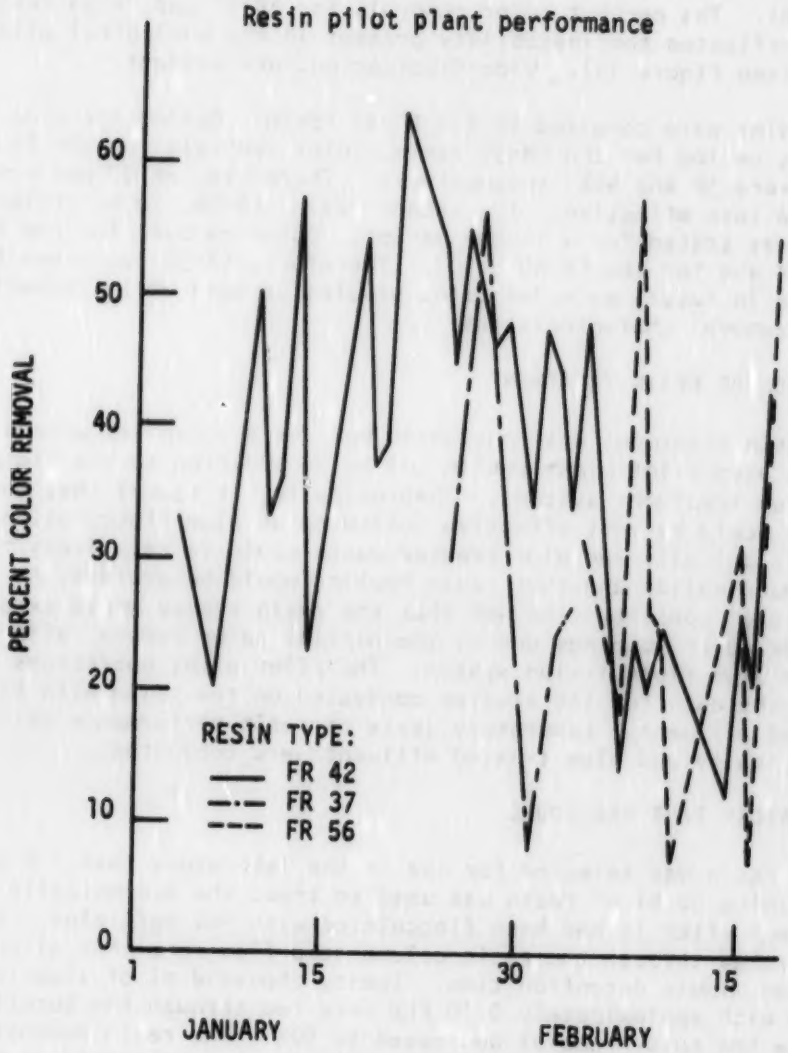
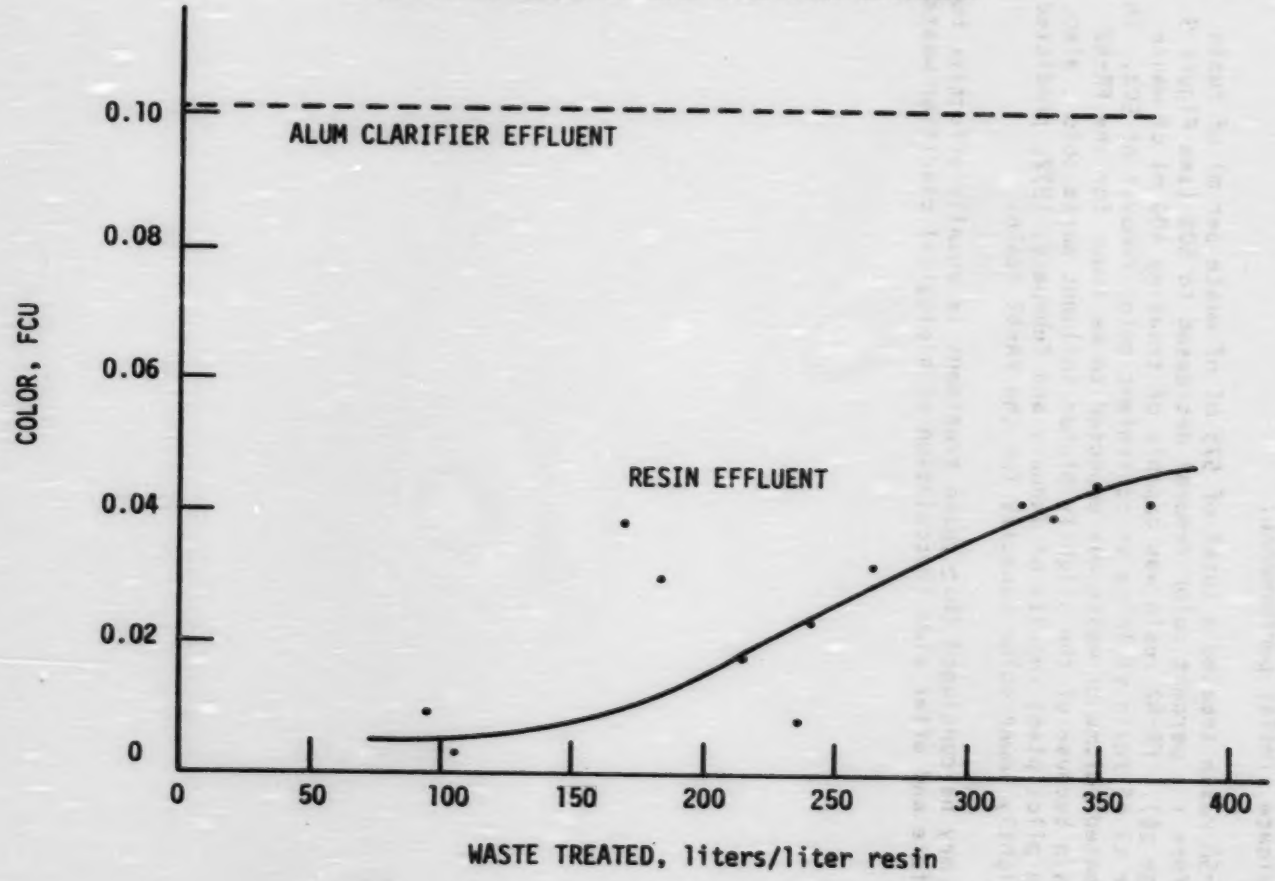


Figure 10

Resin treatment of alum clarifier effluent



used for treating a biologically treated waste with the resultant average of 0.084 FCU (see Figure 9, page 28). The laboratory study of FR-42 resin utilized an alum treated waste with approximately the same amount of color - 0.101 FCU. The test results indicate similar performance.

FR-56 resin treated a total of 575 ml of waste per ml of resin before the percent color removal decreased to 50% (see Figure 9, page 28). FR-42 resin was capable of treating 400 ml of waste per ml of resin yielding an equivalent color removal of 50%. The treated volume of waste was expected to be lower for the FR-42 resin because of the slightly higher influent waste color; also, the pilot plant results of January and February, 1972, predicted a slightly lower color capacity for the FR-42 resin.

It may be concluded that resin treatment is equally effective both before and after alum flocculation of biological clarifier waste.

SECTION V

DESCRIPTION AND OPERATION OF PILOT PLANT

The pilot plant system was designed as a carbon catalyzed biological system for secondary treatment. For tertiary treatment, an on-site alum pilot plant system was evaluated. An alternative method to upgrade the waste effluent from the biological pilot plant with the use of resin adsorption columns was also investigated.

TREATMENT SYSTEM - BIOLOGICAL

The biological pilot plant employed at Cone Mills was a completely mixed, activated sludge system as depicted in Figure 11. Untreated waste from Cone Mills was continuously collected in a small holding tank used to provide equalization and storage for the feed pump. The waste feed pump was a peristaltic type with a variable speed drive and was used to provide flow to the catalyzed aeration system at 150 - 200 milliliters per minute. The aeration system consisted of three catalyzed biological reactors operating in series.

Each of the three aeration vessels had a volume of 125 liters, yielding a detention time of 10.4 - 13.9 hours in each stage, depending on the flow rate. To catalyze the biological reaction, 625 grams of carbon were initially placed in each aeration vessel. Aeration was provided to each reactor via a rotameter for air flow control and a set of three fixed porous stone diffusers located in the bottom of each aeration vessel.

In order to maintain the high concentration of biological solids necessary for biodegradation, a settling tank was provided following the third stage aeration tank. Effluent from the third stage aeration tank was discharged to the cone shaped biological clarifier (settling tank) where the suspended solids consisting primarily of micro-organisms were allowed to settle. To insure these solids did not adhere to the walls of this clarifier, an automatic scraping device was provided. The clarified supernatant was passed on to the alum or resin system for further treatment. The suspended solids collected at the bottom of the clarifier were returned to the first aeration tank to maintain the desired micro-organism concentration in the system. To control the return sludge rate, an off-time clock was used to actuate a small centrifugal pump (see Figure 11) at intervals of 15 minutes. Periodically, biological sludge was wasted from the clarifier when biomass concentrations became too high, and after stable operating conditions were obtained, the unit was operated on a continuous 100% recycle.

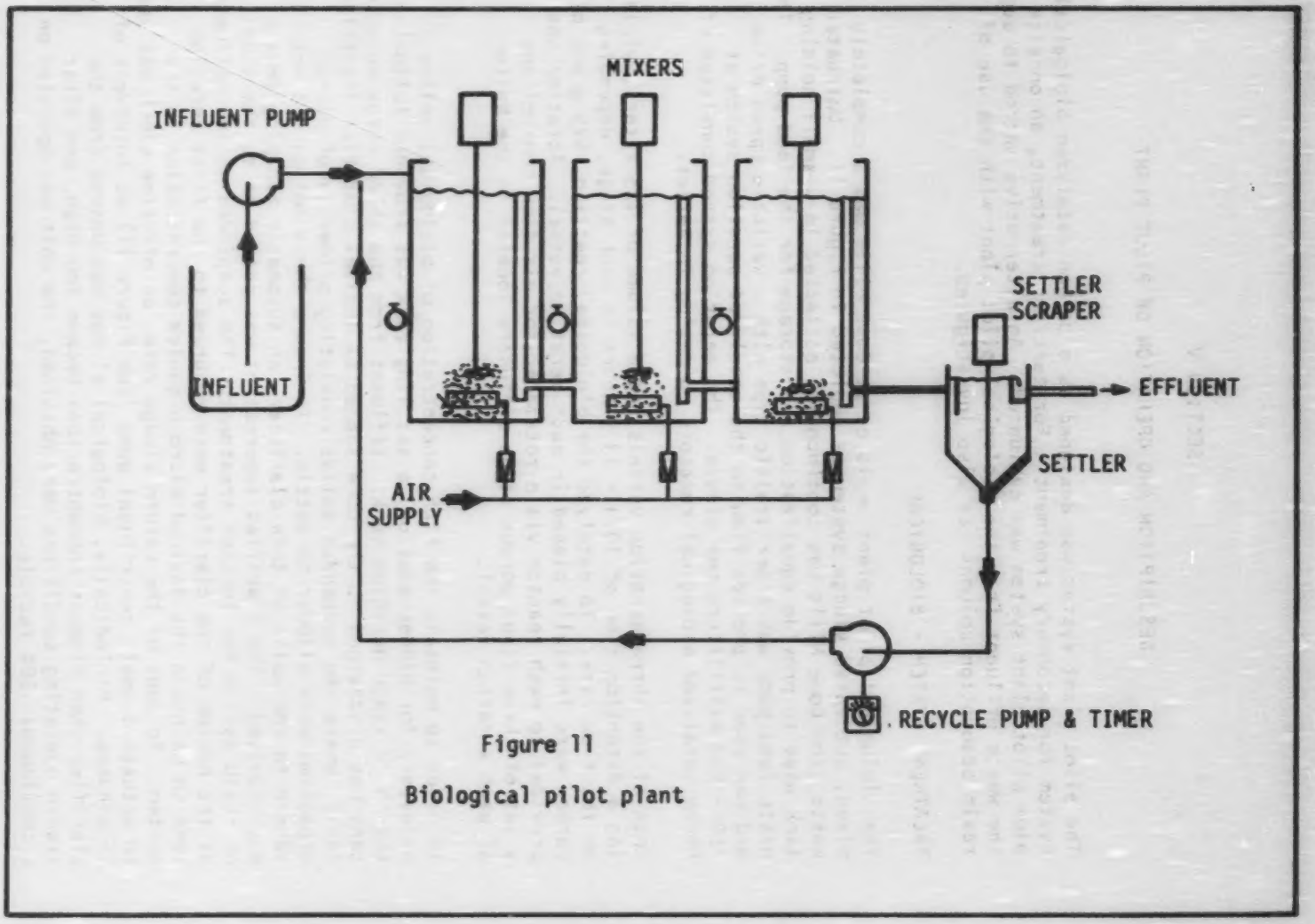


Figure 11

Biological pilot plant

TREATMENT SYSTEM - ALUM

A schematic diagram of the pilot plant is shown in Figure 12. Biologically treated waste from the biological clarifier was mixed with alum and sulphuric acid in the flocculator with a 100-minute detention period. The sulphuric acid was used when required for pH control in the flocculator. The clarified biological effluent now containing aluminum hydroxide sludge at a pH of 6.5 - 7.5 (as adjusted) was then sent to a second clarifier with a 4.9 hour detention period to produce a clear effluent. Pilot plant operations were continuous through the second clarifier. The batch alum recovery operations as described below were conducted manually.

The hydroxide sludge containing influent suspended solids and precipitated phosphates was drawn off daily from the bottom of the clarifier and collected in a receiving tank. The sludge was acidified with concentrated sulphuric acid to dissolve the aluminum hydroxide and recover it as aluminum sulphate. The recovered alum solution was added to the alum feed tank for reuse in the flocculator.

Daily analyses of COD, BOD_5, volatile and total suspended solids, ammonium and phosphate content, color and pH were made of the flocculator influent waste and the clarifier treated effluent.

TREATMENT SYSTEM - RESIN

During the months of June and July, 1972, FR-56 resin was further tested in a pilot plant confirmation study using biological clarifier effluent from the existing Cone biological treatment system. This waste was similar to that from the biological pilot plant.

The resin pilot plant consisted of a glass column 76.2 centimeters high and 2.5 centimeters in diameter, and a feed pump (see Figure 13). A total of 300 ml of resin was utilized in this column. The treated clarifier effluent was pumped downward through the resin bed at a rate of 20 ml per minute. This rate afforded a 15-minute detention time. The column was run 24 hours a day for 7 to 10 days. After this time period, the resin became loaded with contaminant and could not operate at its maximum efficiency. The resin loading was reflected in the simultaneous deterioration of the effluent quality. At this point, the resin was regenerated in the column in a downflow direction.

Several steps were necessary for regeneration (see Figure 13). The first step was to remove solids particles that accumulated on the resin bed during the treatment of clarifier effluent. This was accomplished by backflushing the resin with six liters of water at 200 ml per minute upflow. After backflushing, the adsorbed color was stripped from the resin using five liters of 2% caustic

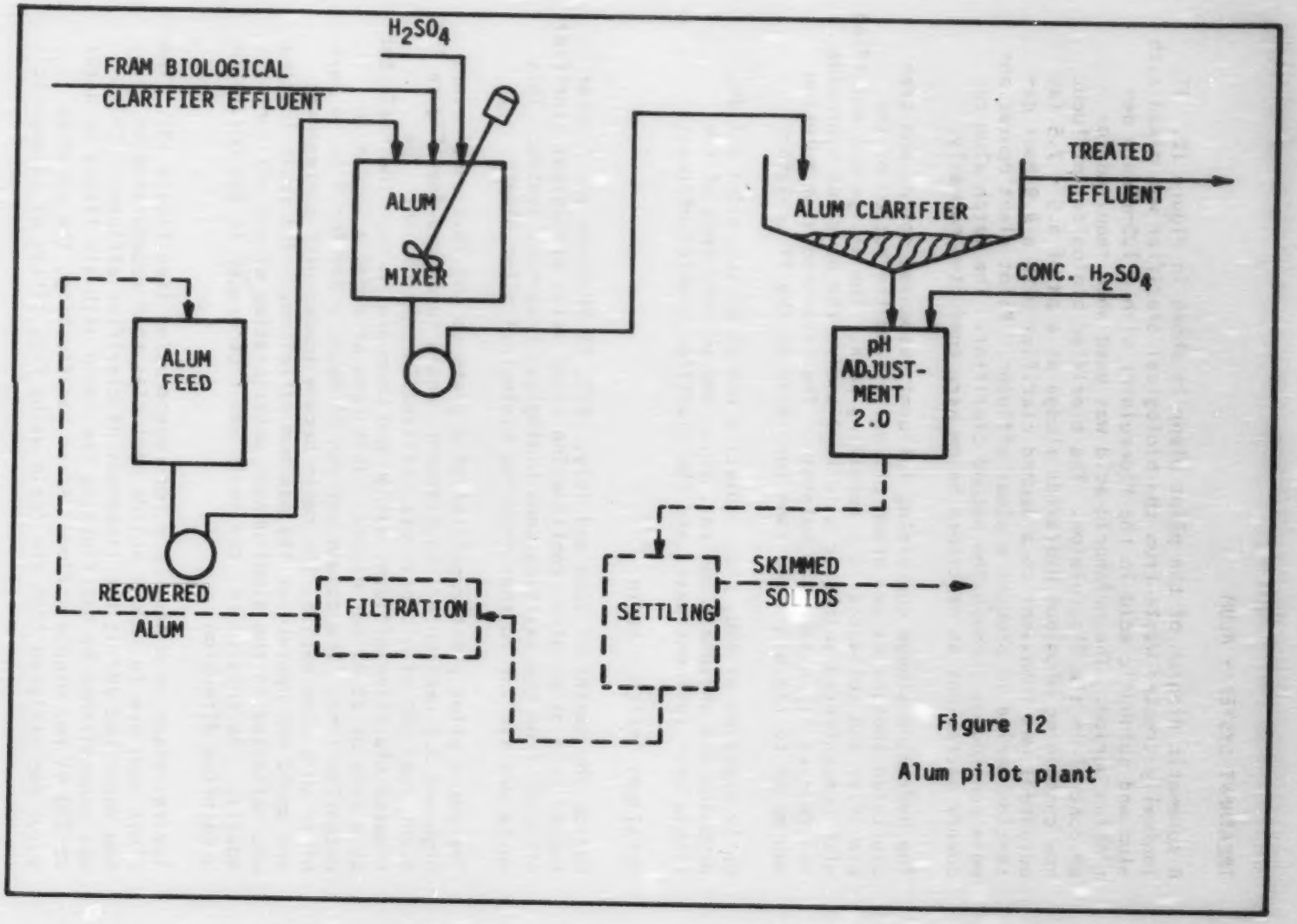


Figure 12

Alum pilot plant

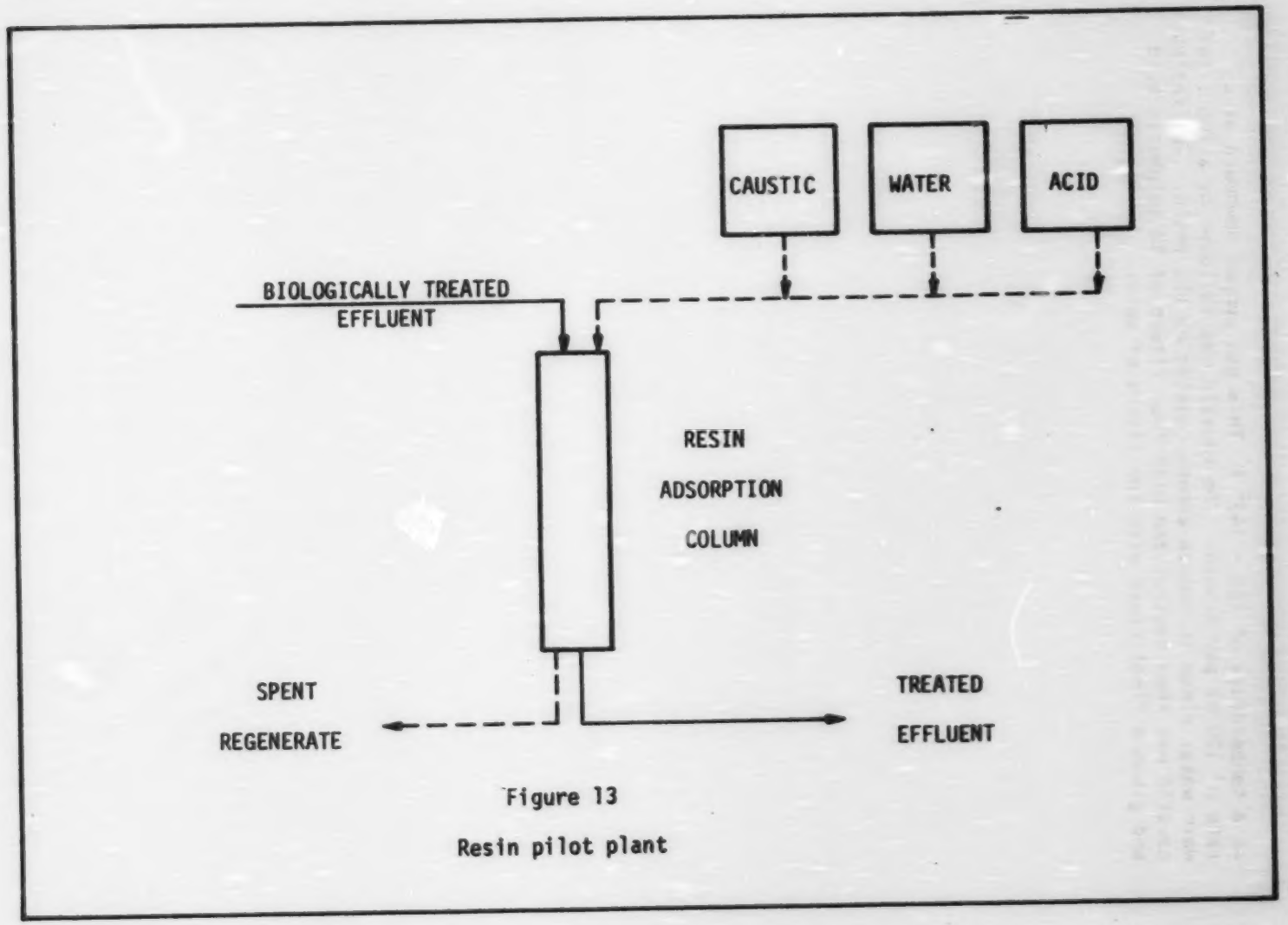


Figure 13

Resin pilot plant

at a temperature of 130 - 140° F. This was pumped downward at a rate of 100 ml per minute. The caustic was followed by a two liter warm water rinse to remove excess caustic on the resin. The residual caustic was then neutralized with four liters of 2% sulphuric acid and given a final rinse with two liters of water.

SECTION VI

PILOT PLANT DATA

Pilot plant operations at Cone Mills can be categorized into three phases. Those phases are described by the following time periods:

Phase I - September 23, 1971 to November 12, 1971

Phase II - November 13, 1971 to March 22, 1972

Phase III - March 23, 1972 to May 25, 1972

In general, biological pilot plant performance was found to be good for Phase I and Phase III; however, many operating difficulties were encountered during Phase II which adversely affected pilot plant performance.

One of the goals of the pilot plant study was to obtain maximum system and process efficiency. Average percent removals of BOD_5, COD, and color for the three phases are shown in Figure 14. The drastic decrease in removals during Phase II is attributed to biological fouling of aerators in the reactors, causing plugging and oxygen deficiencies. With the installation of new aerators prior to Phase III, immediate gains in process performance were realized. Sludge wasting was considered to be an influencing factor in both system and process efficiency.

Table 6 was compiled from data from the last part of Phase III and reflects the optimum system and process performance that were achieved by the biological pilot plant alone.

PHASE I

Fram personnel initiated Phase I of the program by the installation of the pilot plant at Cone Mills on September 23, 1971. Data were collected throughout Phase I. A comparative analysis of Cone Mills' waste effluent and the biological pilot plant waste indicated improvement in BOD_5 removal (Table 7).

Phase I was characterized by new aerators, no sludge wasting and a detention time of 42 hours in the three reactors. The first reactor (R1) removed the bulk of BOD_5 and color as expected in a staged aeration system. The second and third reactor (R2 and R3) increased the total color removal from the R1 effluent by approximately 50%, while the increase for the BOD_5 removal was approximately 11%. Total BOD_5

Figure 14

Biological pilot plant overall performance

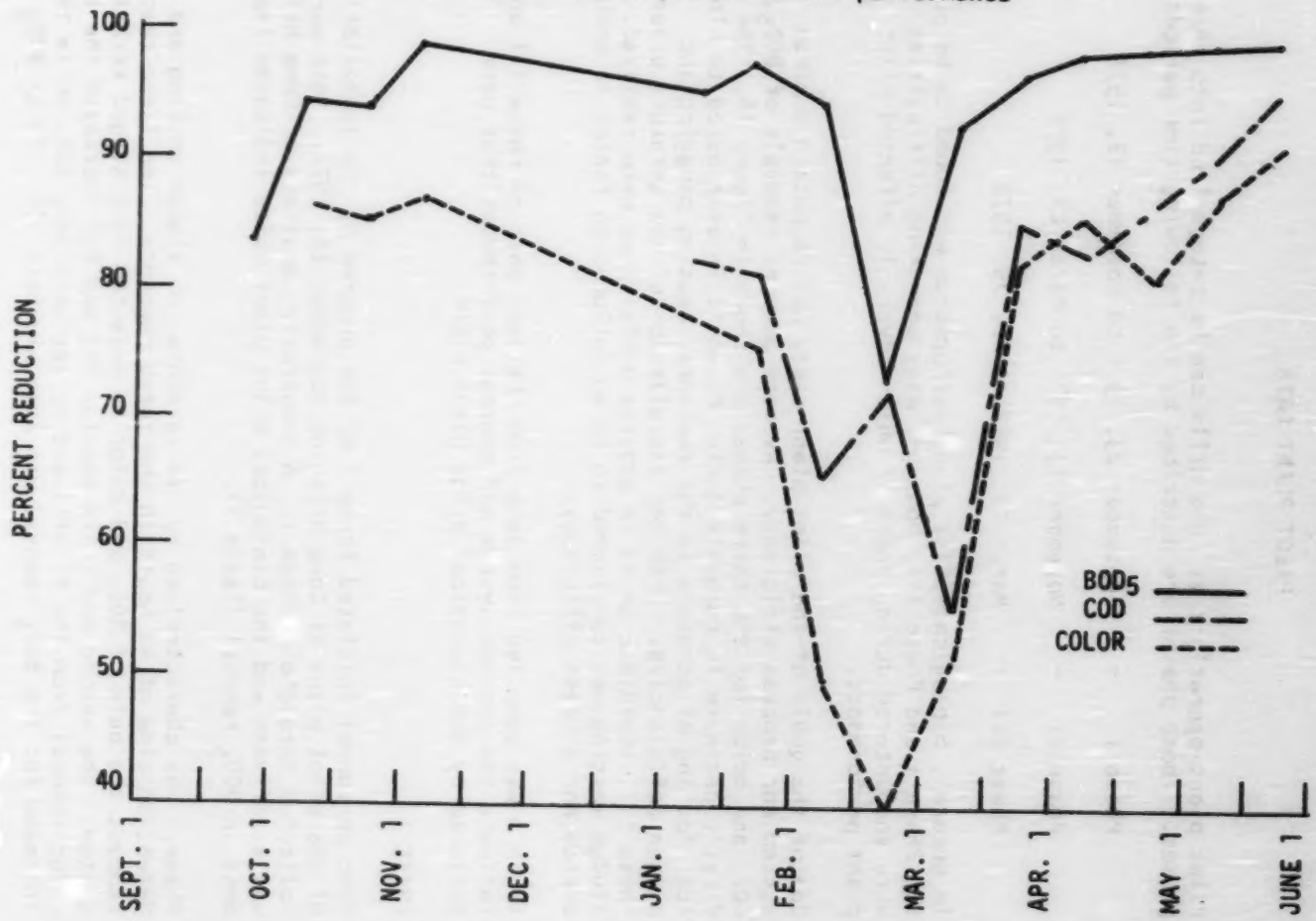


Table 6. BIOLOGICAL PILOT PLANT - OPTIMUM PERFORMANCE
Data for phase III, period 3

Parameter	Median	95% Percentile	Average removal, %
COD, mg/l	135	185	91
BOD_5, mg/l	4.5	6.2	99
SS, mg/l	27	54	-
Nitrogen as ammonia, mg/l	2.0	5.2	76
Phosphate, mg/l	1.7	4.0	-
Color, FCU	0.130	0.161	90
pH	7.6	8.15	-

Table 7. COMPARISON OF PILOT PLANT AND MAIN PLANT EFFLUENTS
Phase 1

Parameter	Cone effluent	Fram effluent
BOD_5, mg/l	39.0	6
SS, mg/l	56.0	35
Phosphate, mg/l	1.5	1.5
Color, FCU	0.279	0.198

and color removals for the three reactors were 98.1% and 76.5%, respectively (Table 8). Additional color and BOD_5 removal were achieved in the biological and alum clarifiers as described later in this report.

Although the low dissolved oxygen concentration in the first reactor did not inhibit growth of the micro-organisms, it did limit the amount of biodegradation that occurred. With the installation of new aerators prior to Phase II, the dissolved oxygen (D.O.) concentration was maintained at a higher level and, as a result, a better BOD_5 removal was obtained.

PHASE II

The system was operated under conditions identical to those of Phase I.

In mid-December, 1971, a sudden increase in color and BOD_5 in the effluent from the biological system was noted. Analytical tests determined that a shock loading of metallic ions had been received; chromium and zinc seemed to have killed the micro-organisms. The existing waste treatment plant did not seem to be affected in the same manner. Because of this upset, the entire pilot plant was flushed and restarted in early January, 1972. The unit was operated as before except that sludge was wasted occasionally.

BOD_5, COD, and color reductions immediately following start-up were satisfactory; however, they rapidly began to decrease after two weeks of operation (see Figure 14, page 38). By late February, 1972, BOD_5 reductions had dropped to 75%, while color reductions had dropped to 40%. COD removal was as low as 55%. The D.O. levels in the system were also noted to be lower than during Phase I. To determine if contaminated carbon was the source of trouble, additional carbon was added to the reactors. No improvement in treatment was noted following addition of the carbon.

It was decided to shut the system down, completely clean out the pilot plant, and replace the aerators and carbon. Inspection of the old aerators showed them to be partially plugged. The used carbon was found to be neither fouled by sludge nor by heavy metals.

The system was restarted for Phase III.

PHASE III

Phase III operations were begun the end of March, 1972, after completely cleaning the pilot plant and replacing the aerators and carbon.

Table 8. BIOLOGICAL PILOT PLANT DATA - PHASE I
Average values

Parameter	Influent	Reactors 1	2	3	Biological Clarifier effluent
BOD_5, mg/l	443	60	21	8.5	-
D.O., mg/l	2.1	0.6	1.3	3.2	-
Color, FCU	0.932	0.465	0.283	0.219	0.198
Nitrogen, mg/l	11.89	-	-	-	2.82
Phosphate, mg/l	2.1	-	-	-	1.5

The sudden increase in BOD_5, COD, and color removals was dramatic, reaching levels experienced during Phase I (see Figure 14, page 38).

Because of changing operating conditions experienced during Phase III, it may be subdivided into three periods. The periods are characterized by the following parameters:

Period 1	A total retention time of 31 hours in the reactors
Period 2	Clean aerators identical in number and size to those of Phase I
Period 3	Periodic sludge wasting

The second period is identical to Period 1 except that three aerators were added to the first reactor to increase the D.O. level. The third period is identical to Period 2 except that sludge was wasted on a regular basis. Each period's operating conditions represent an improvement over the previous period, in regards to removal efficiencies (see Table 9).

Period I of Phase III compared to Phase I shows improvements in BOD_5 and color reductions (Table 9). Clean identical equipment was used for both time intervals. The variables were total detention time and periodic sludge wasting. Since the lower detention time would affect a system negatively, it was assumed that the periodic sludge wasting was responsible for the increase in BOD_5 and color removal. The first reactor (R1) showed marked improvement in BOD_5 and color reductions (4.3% and 7.5%, respectively). While the total BOD_5 removal did not increase significantly, total color removal increased by 4.8%. The D.O. levels were similar for these two evaluation periods.

The low D.O. concentration in R1 was thought to prevent complete biological degradation. In Period 2, three aerators were added to the first reactor (R1). With the additional aerators, the D.O. level in R1 nearly doubled (Table 9, page 44). Color removal in R1 jumped from 57.5% (Period 1) to 80.0% (Period 2), resulting in a total color removal increase of 3.8% from the three reactors. BOD_5 removals in R1 increased 5.7% in Period 2. Because no additional air source was added, it was concluded that the original air diffusers had become ineffective. Upon inspection at a later date, the air diffusers were found to be fouled with biological growth.

Up until late March, sludge wasting was performed on a limited basis only. The advantages of periodic sludge wasting were seen in Period 1. The benefits of regular sludge wasting were realized in Period 3.

Table 9. PERFORMANCE OF BIOLOGICAL REACTORS

Parameter	Phase I	Phase III		
		Period 1	Period 2	Period 3
BOD_5, % removed				
Reactor R1	86.5	90.8	96.5	96.8
Reactor R2	8.8	6.0	1.8	2.1
Reactor R3	2.8	1.5	0.5	0.3
Total	98.1	98.3	98.8	99.2
Color, % removed				
Reactor R1	50.0	57.5	80.0	86.5
Reactor R2	19.6	15.0	2.3	3.2
Reactor R3	6.9	8.8	2.8	0.9
Total	76.5	81.3	85.1	90.6
D.O., mg/l				
Influent	2.1	2.0	3.0	2.2
Reactor R1	0.6	0.6	1.1	1.0
Reactor R2	1.3	2.2	3.3	2.4
Reactor R3	3.2	3.3	3.8	3.6
COD % removed				
Total	-	84.5	89.6	95.4

During Period 3, the pilot plant was operated under conditions identical to those of Period 2, except that sludge was wasted on a regular basis. The improvements in BOD_5 reduction were slight, increasing BOD_5 removal by 0.3%. As shown before, in comparing the benefits of sludge wasting in Phase I (no sludge wasting) and Period 1 (periodic sludge wasting), color removal was the most sensitive parameter to the amount of sludge wasted. The color removal for Period 3 increased 6.5% in R1, giving a total overall color removal increase of 5.5% over Period 2.

The operating conditions imposed during Period 3 are considered to be an optimum level. Period 3 most closely simulated the design parameters of an actual plant, including sufficient aeration and regular wasting of activated sludge. Figures 15 through 21 graphically illustrate the percent occurrences of concentration values for the raw, untreated waste and the biological clarifier effluent.

ALUM PILOT PLANT RESULTS

The biological pilot plant effluent was further treated in the alum pilot plant system. This additional system was recommended to increase the removal of the phosphates and reduce the color content in the Cone effluent.

The actual performance of the alum pilot plant over a period of three months (March 23 to May 25, 1972) was close to that predicted in the preliminary laboratory studies. Table 10 summarizes the average influent and effluent characteristics during this period using alum concentrations of 300 mg/l. Reductions in BOD_5 and COD were approximately 38% and 19%, respectively. Phosphate content of the waste was reduced consistently to 0.1 and 0.2 mg/l levels, regardless of the influent concentration (varying from 0.2 to 6.4 mg/l). The low final concentration was expected since the precipitated aluminum phosphate has a constant low solubility.

Color removal was found to be more variable and complex. Analysis of the clarifier effluent color with respect to the clarifier pH indicates a slight dependence of color removal on pH. Referring to Figures 22 and 23, fluctuations in influent and effluent color versus the final effluent pH were apparent. These fluctuations appeared to fall within certain limits. In order to normalize these variations, approximate limits were established and the limit averages taken to yield average color values at various clarifier pH's. Average percent color removal versus clarifier pH is shown in Table 11. Average color removals varied from 30% to 41% for clarifier pH's of 7.25 and 6.25, respectively, yielding a pale yellow effluent. Treatment schemes employing lower clarifier pH's for added color removal were considered uneconomical because of the large acid requirements (see titration curve, Figure 24).

Figure 15

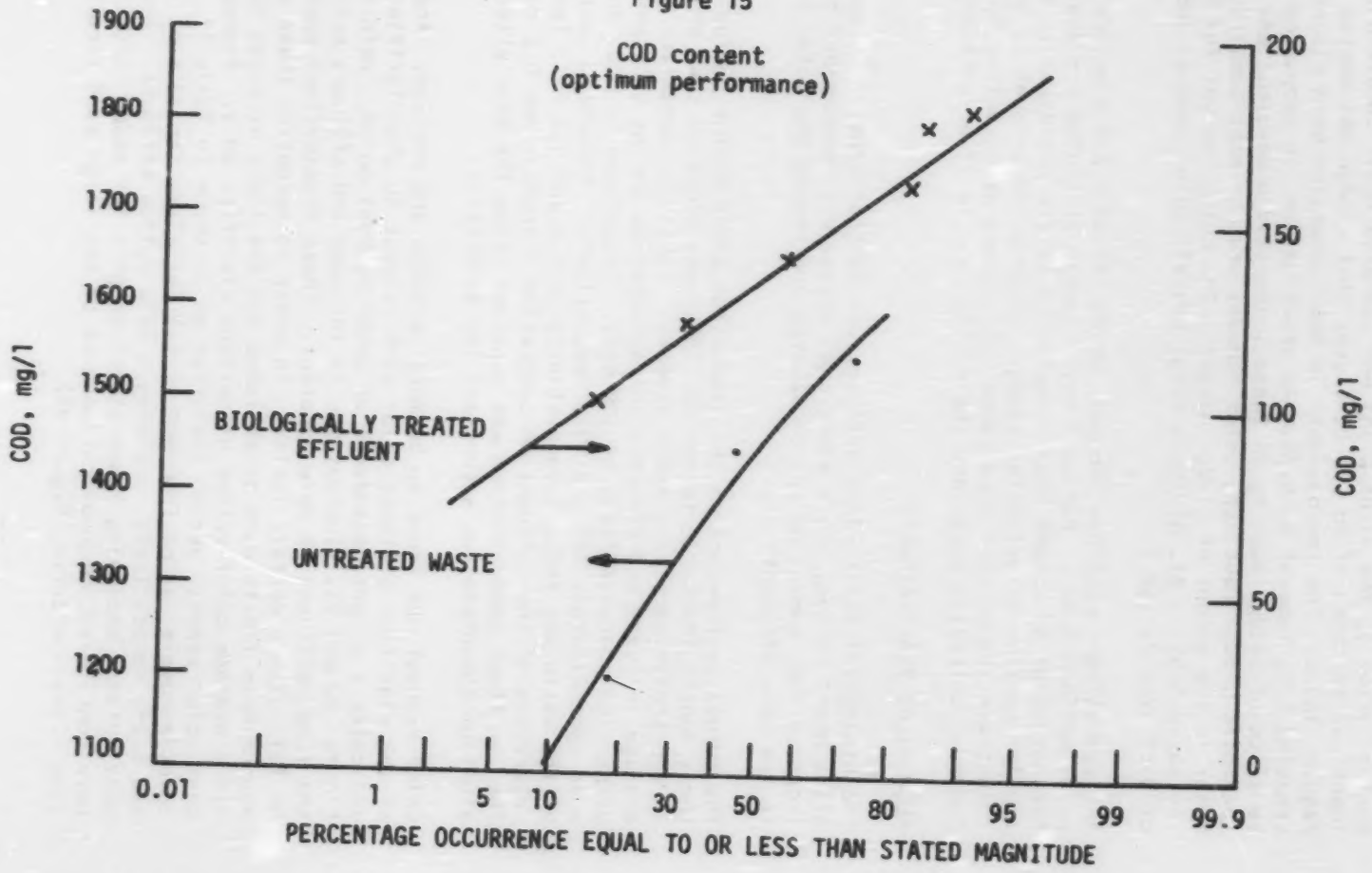

COD content
(optimum performance)
BIOLOGICALLY TREATED
EFFLUENT
UNTREATED WASTE
COD, mg/l
1900
1800
1700
1600
1500
1400
1300
1200
1100
200
150
100
50
0
0.01
1
5
10
30
50
80
95
99
99.9
PERCENTAGE OCCURRENCE EQUAL TO OR LESS THAN STATED MAGNITUDE

Figure 16

BOD content
(optimum performance)

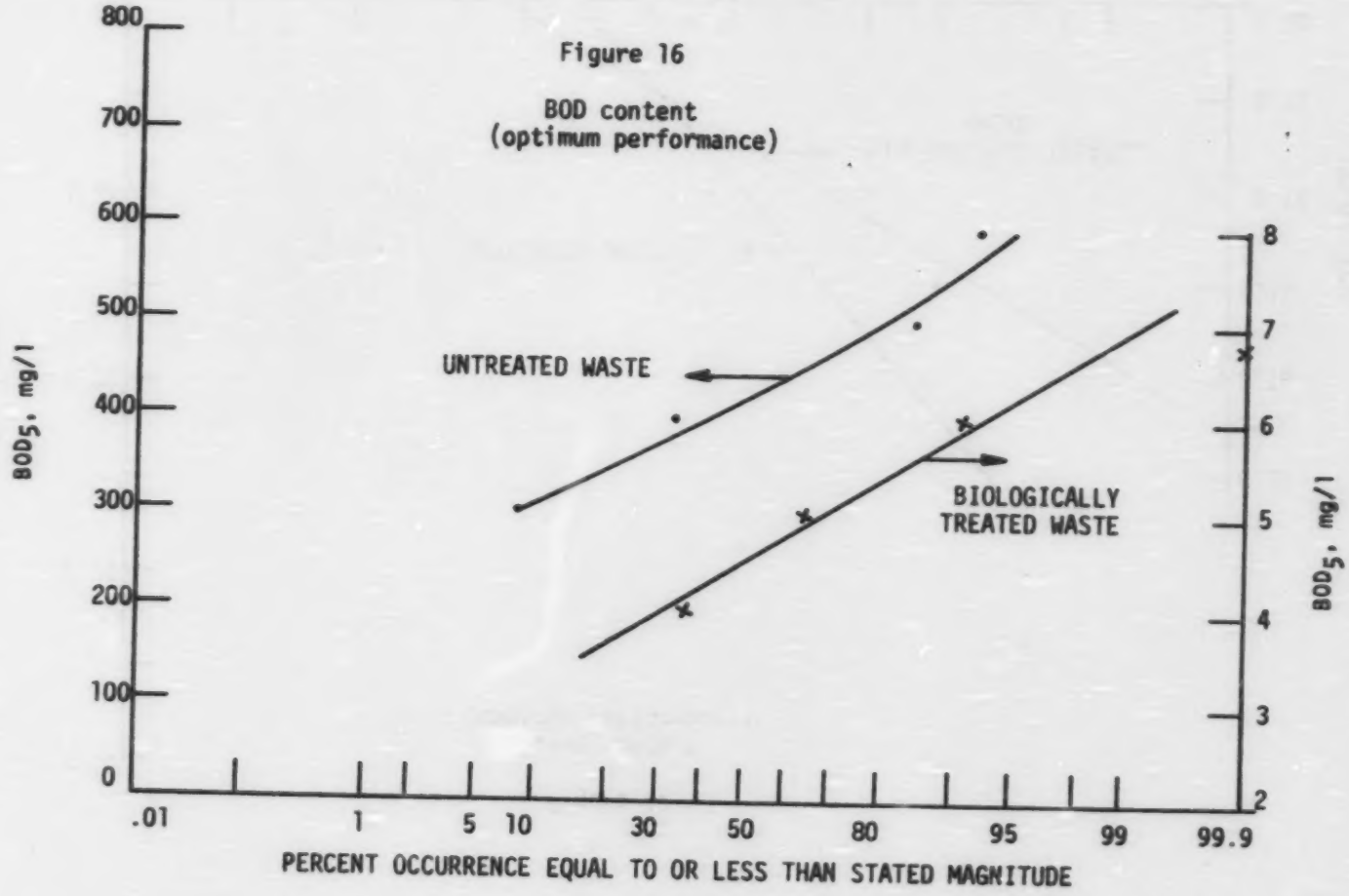


Figure 17

Color content
(optimum performance)

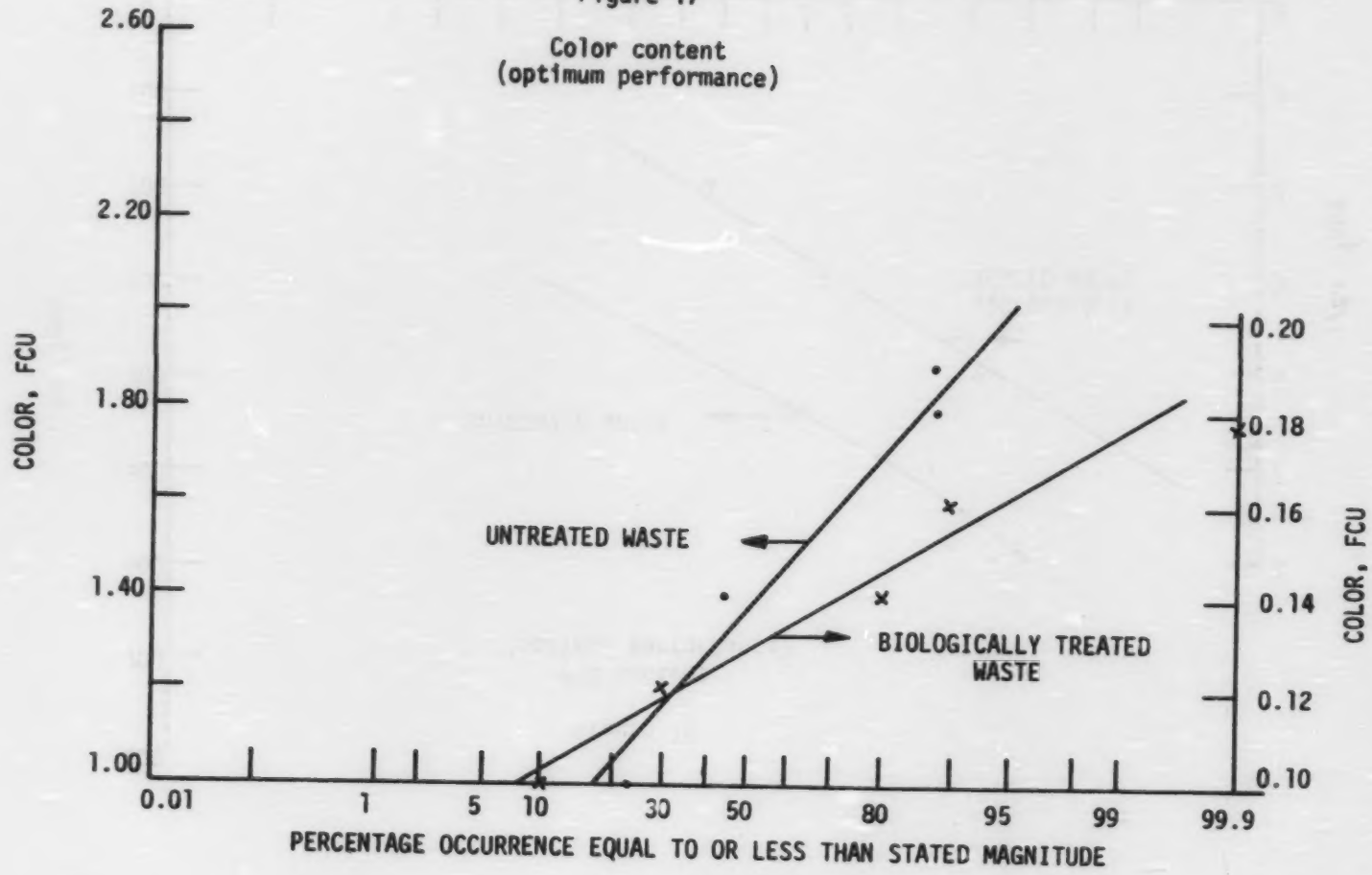


Figure 18

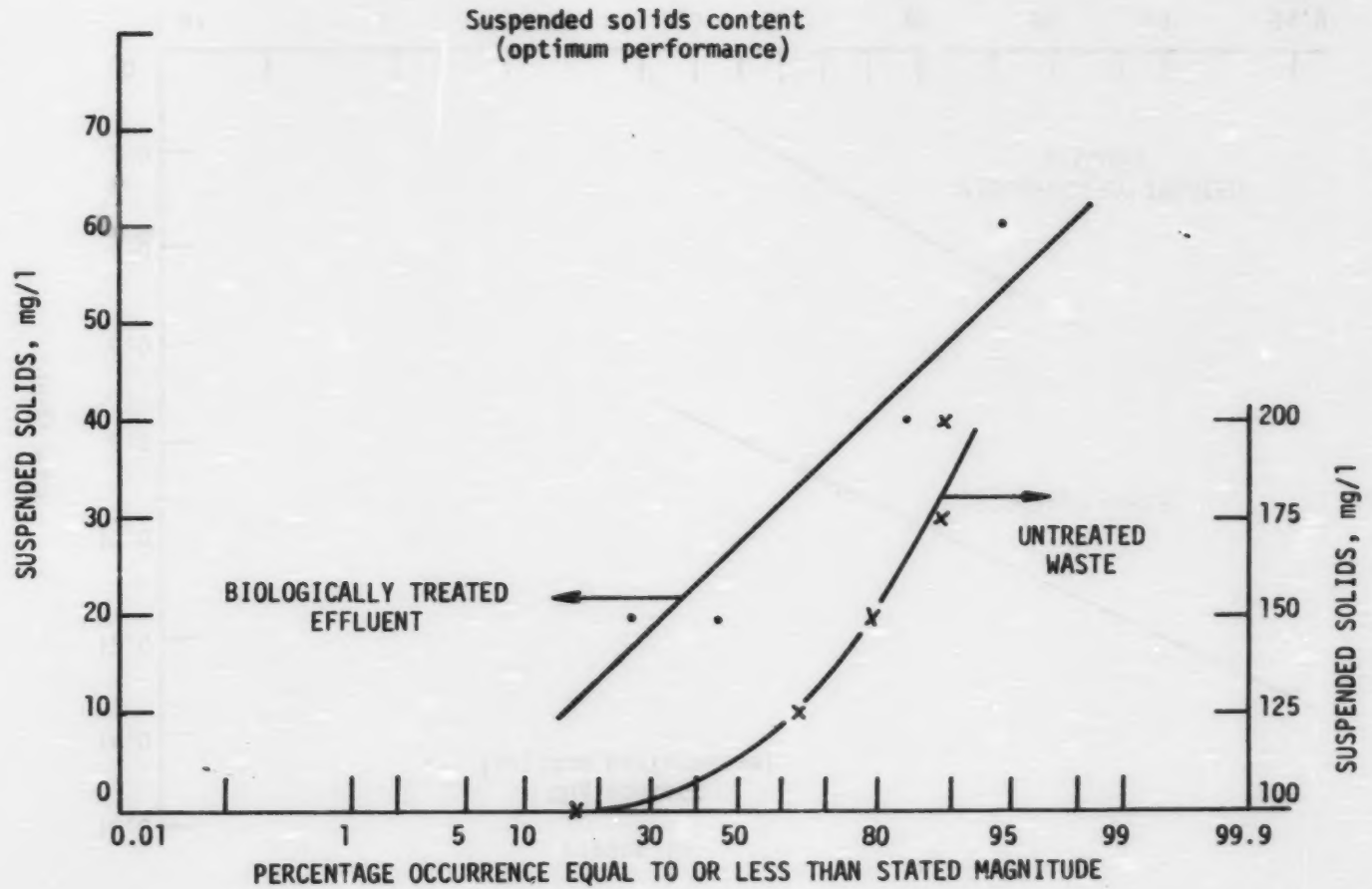

Suspended solids content
(optimum performance)
SUSPENDED SOLIDS, mg/l
70
60
50
40
30
20
10
0
200
175
150
125
100
SUSPENDED SOLIDS, mg/l
BIOLOGICALLY TREATED
EFFLUENT
UNTREATED
WASTE
0.01
1
5
10
30
50
80
95
99
99.9
PERCENTAGE OCCURRENCE EQUAL TO OR LESS THAN STATED MAGNITUDE

Figure 19

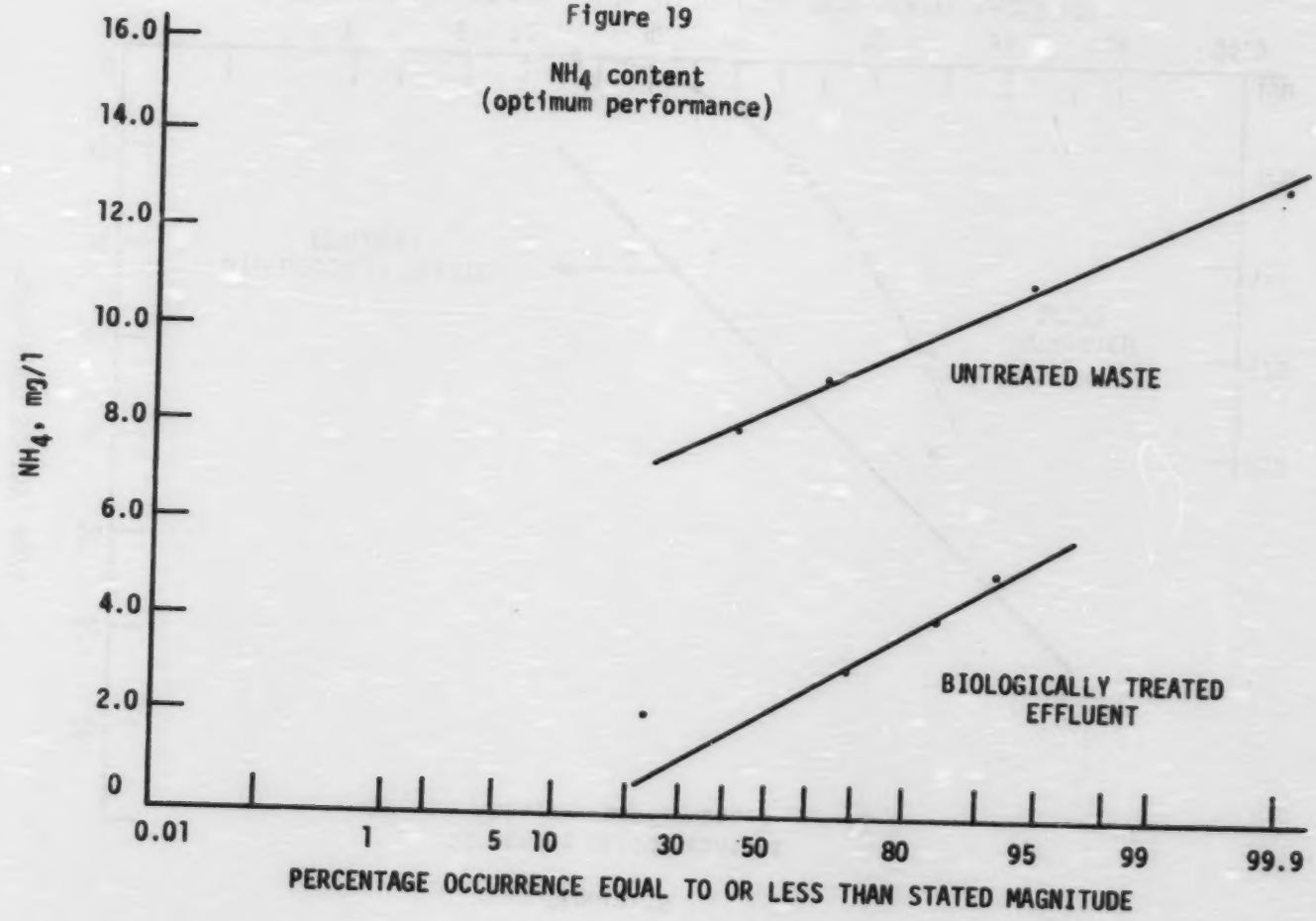

NH4 content
(optimum performance)
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0
NH4, mg/l
UNTREATED WASTE
BIOLOGICALLY TREATED
EFFLUENT
0.01
1
5
10
30
50
80
95
99
99.9
PERCENTAGE OCCURRENCE EQUAL TO OR LESS THAN STATED MAGNITUDE

Figure 20

Phosphate content
(optimum performance)

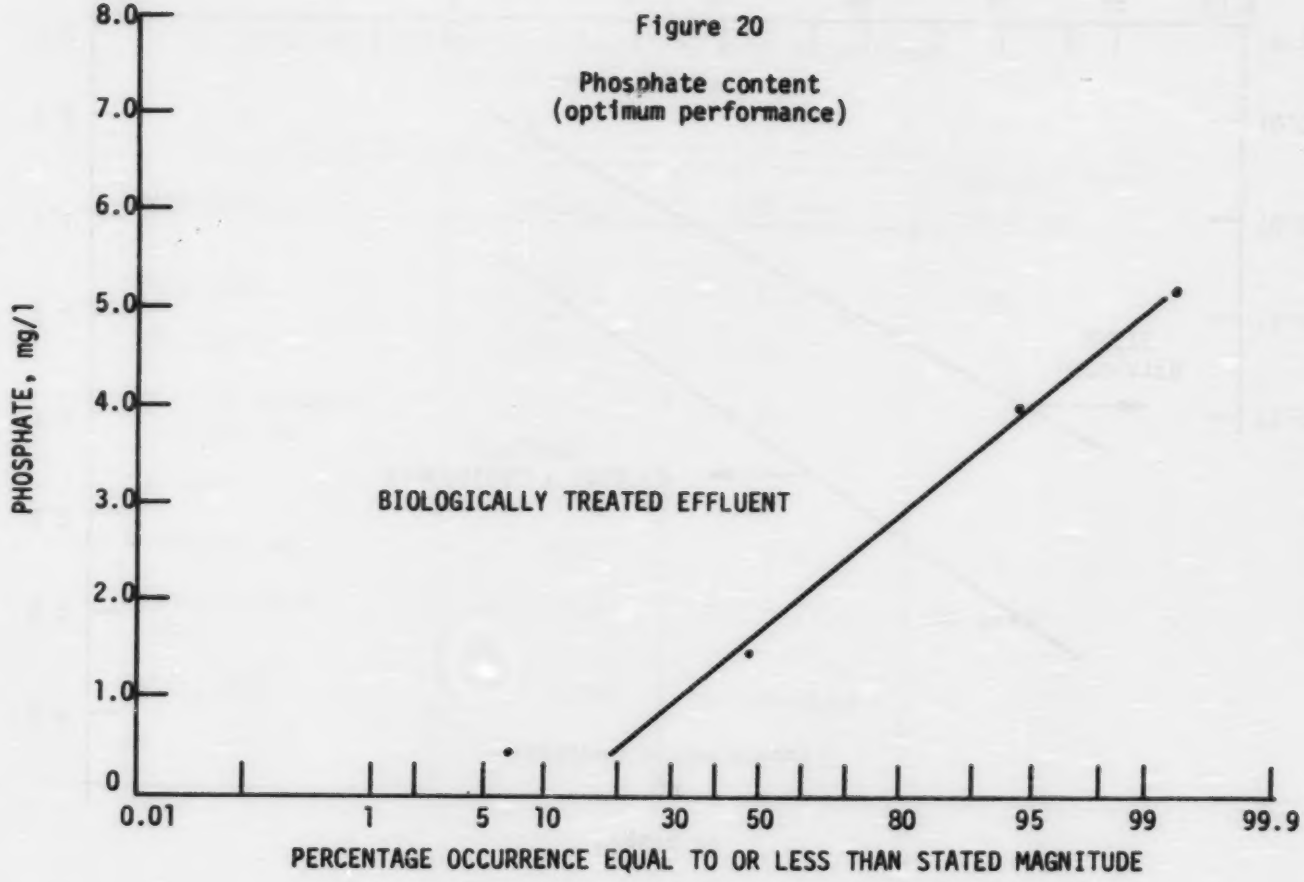


Figure 21

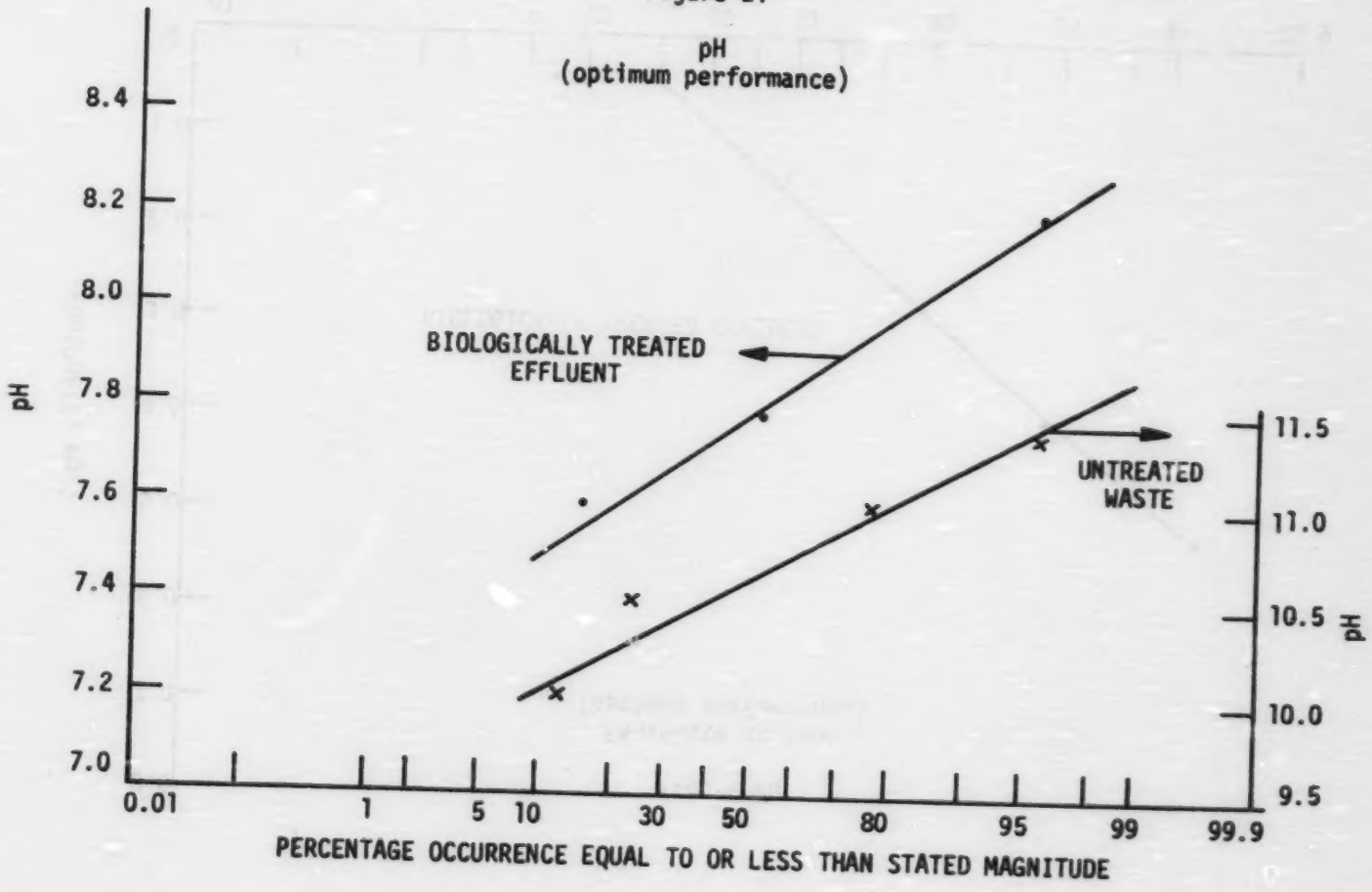

pH
(optimum performance)
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
pH
BIOLOGICALLY TREATED
EFFLUENT
UNTREATED
WASTE
11.5
11.0
10.5
10.0
9.5
pH
0.01
1
5
10
30
50
80
95
99
99.9
PERCENTAGE OCCURRENCE EQUAL TO OR LESS THAN STATED MAGNITUDE

Table 10. AVERAGE PERFORMANCE OF ALUM PILOT PLANT
Alum dosage = 300 mg/l

Parameter	Influent	Effluent	Percent reduction
BOD_5, mg/l	10	6.2	38
COD, mg/l	161	130	19
Volatile suspended solids, mg/l	31	26	16
SS, mg/l	32	39	
Nitrogen, mg/l	5.3	5.5	0
Orthophosphate, mg/l	0.2 - 6.4	0.1 - 0.2	Up to 97
Color, FCU	0.208	pH dependent	
pH	5.0 - 7.8	As adjusted	

Figure 22

Alum clarifier influent color versus clarifier pH
data taken 3/24/72 thru 5/25/72

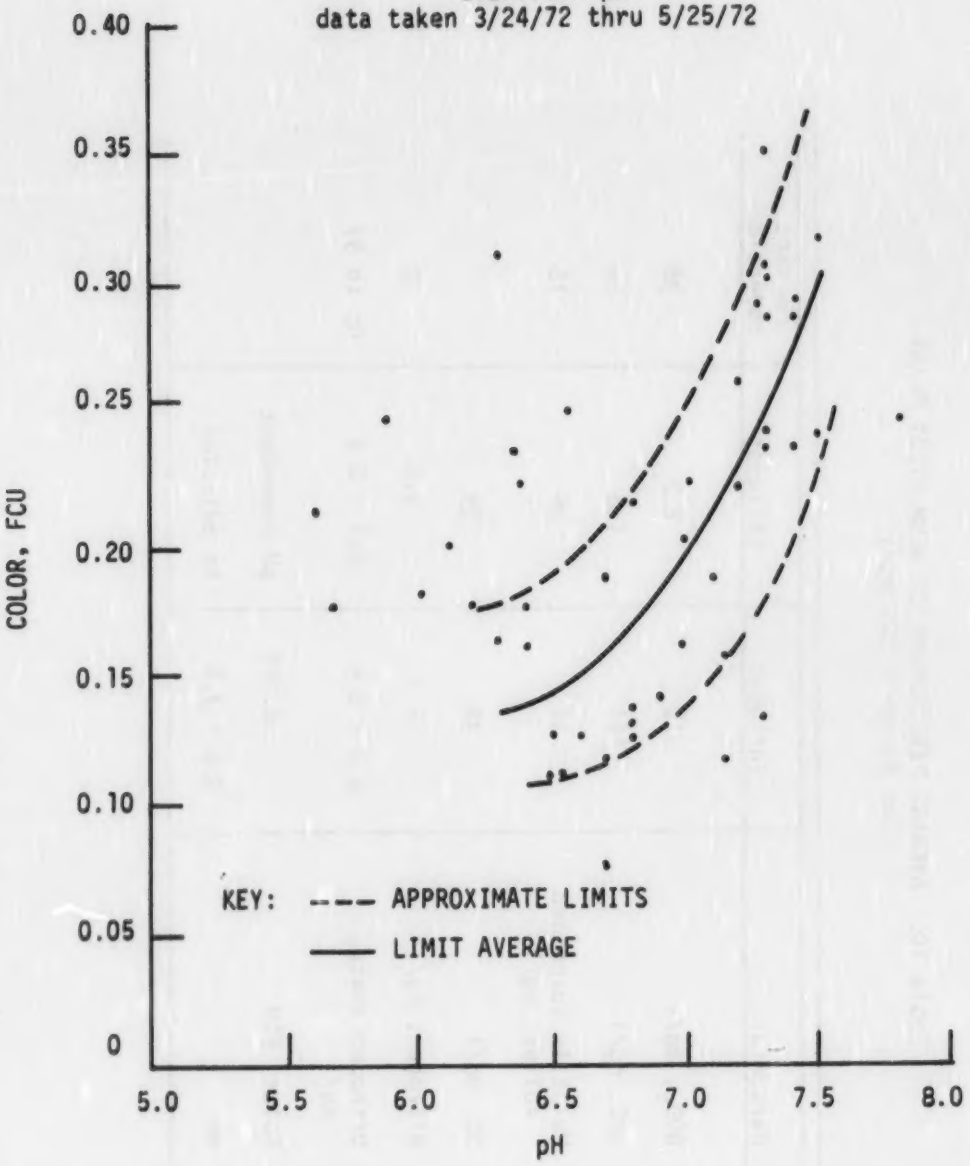


Figure 23

Alum clarifier effluent color versus
clarifier pH
(300 ppm alum)
data taken 3/24/72 thru 5/25/72

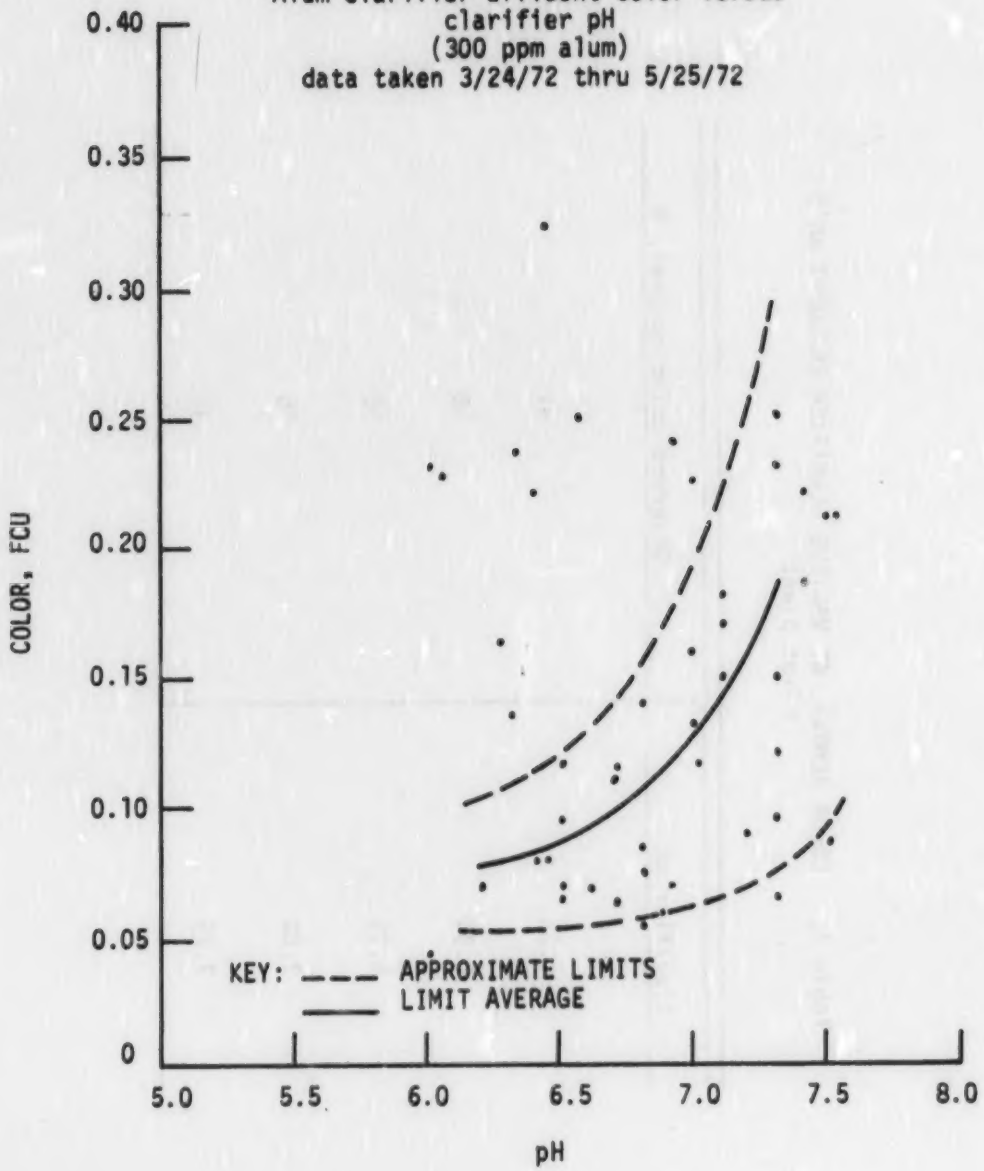
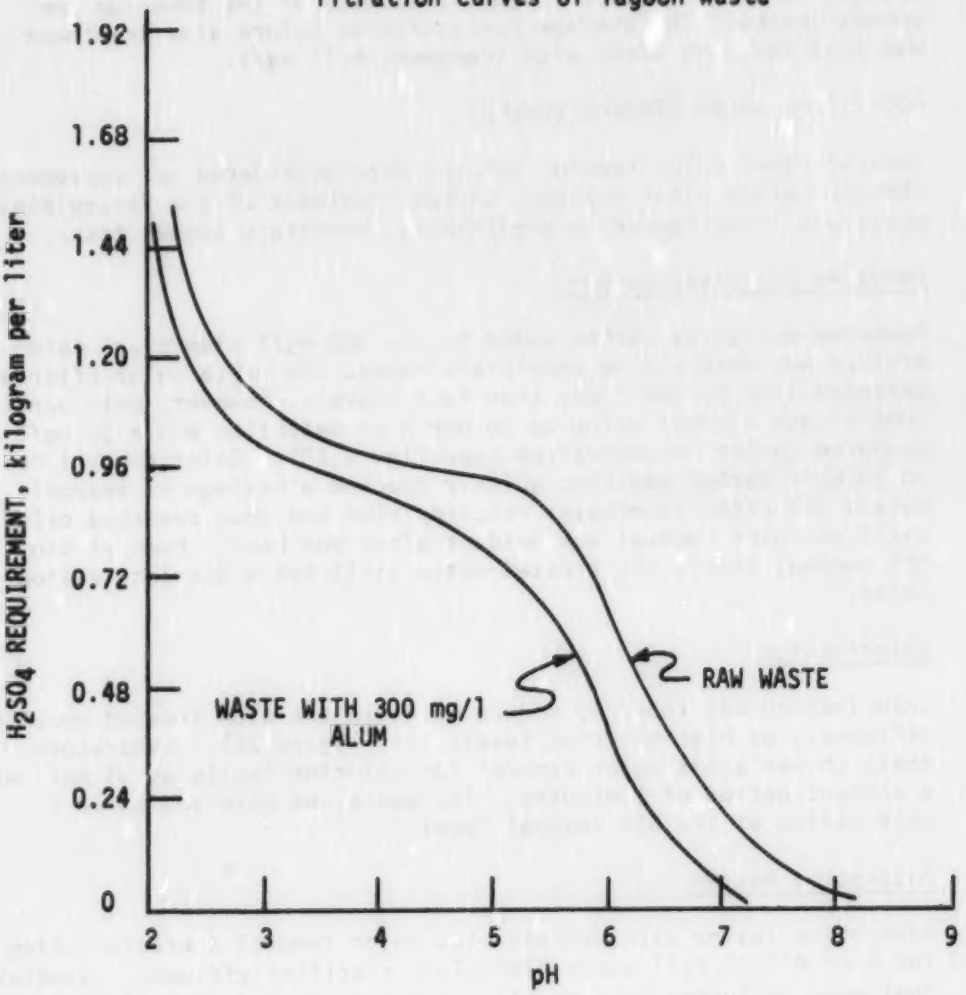


Table 11. COLOR REMOVAL AT VARIOUS CLARIFIER EFFLUENT pH'S
Pilot plant

Clarifier pH	Observed color removal, %
6.25	41
6.50	40
6.75	39
7.00	35
7.25	30

Figure 24

Titration curves of lagoon waste



An increase in the total suspended solids content was observed across the clarifier (refer to Table 10, page 53). The increase of 12 mg/l was caused by a carryover of aluminum hydroxide floc to the effluent (corresponding to a 46 mg/l alum loss). Although pilot plant operations did not include the use of polyelectrolytes, laboratory tests have indicated that 5 mg/l of a cationic polyelectrolyte markedly decreases the settling time and solids overflow.

No reductions in ammonia were observed for the alum coagulation system, as expected, due to the solubility of the ammonium compounds formed. The average concentration before alum treatment was 4.12 mg/l and after alum treatment 4.11 mg/l.

ADDITIONAL COLOR REMOVAL SCHEMES

Several other color removal schemes were considered to supplement the alum pilot plant system. Carbon treatment of the flocculated waste was investigated in preliminary laboratory shaker tests.

Powdered Activated Carbon

Powdered activated carbon added to the 400 mg/l alum plus waste mixture was observed to completely remove the waste color after an extended time period (less than four hours). However, only partial removal was evident using up to one hour detention and a 50 mg/l powdered carbon concentration (see Figure 25). Color removal due to 50 mg/l carbon addition quickly reached a maximum of approximately 32% after 10 minutes reaction time and then desorbed color until no color removal was evident after one hour. Even at the 32% removal level, the treated waste still had a distinct yellow color.

Chlorination

Chlorination was found to reduce color in the alum treated waste significantly at high chlorine levels (see Figure 26). Laboratory tests showed a 63% color removal for chlorine levels of 48 mg/l with a contact period of 5 minutes. The waste was observed to be a pale yellow at the 63% removal level.

Adsorptive Resins

Adsorptive resins also demonstrated color removal characteristics for Cone Mills' full scale biological clarifier effluent. Studies that were performed by Cone Mills are discussed in detail on page 63.

Figure 25

Carbon adsorption of color
during alum flocculation
(50 mg/l carbon)

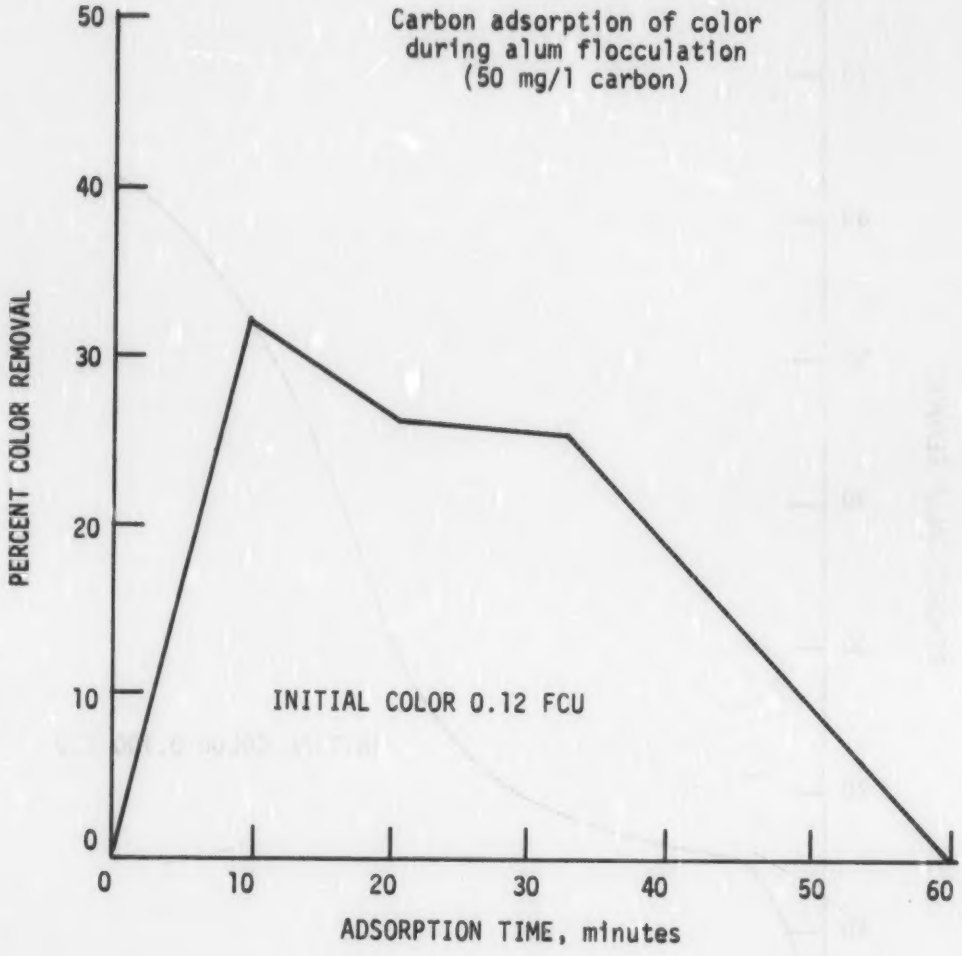
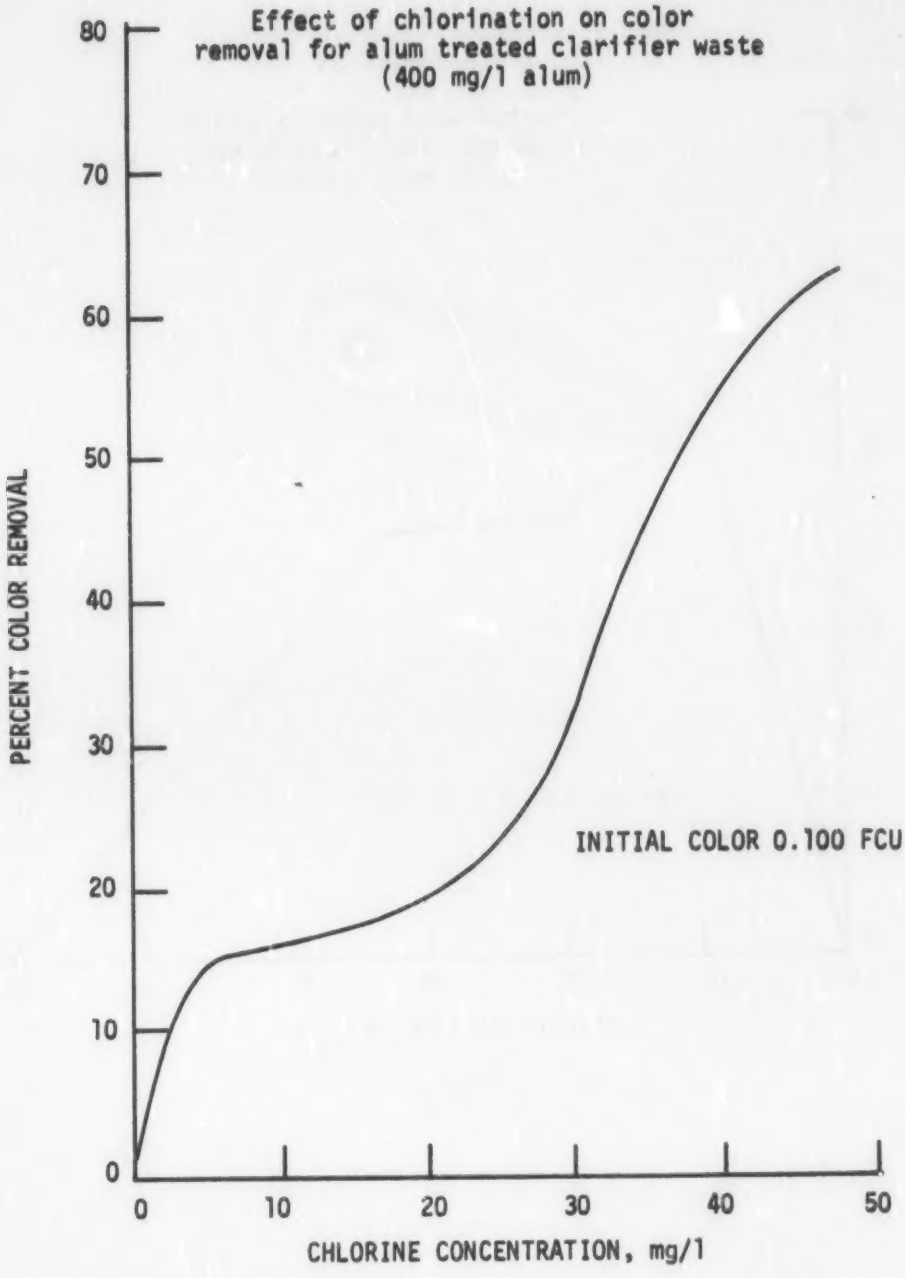


Figure 26


Effect of chlorination on color
removal for alum treated clarifier waste
(400 mg/l alum)
PERCENT COLOR REMOVAL
80
70
60
50
40
30
20
10
0
INITIAL COLOR 0.100 FCU
0
10
20
30
40
50
CHLORINE CONCENTRATION, mg/l

RESIN PERFORMANCE

A resin pilot plant study was performed in June and July, 1972 to evaluate the performance of FR-56 resin (selected in the previous study). During this period, the Cone Mills' biological treatment system performance was stable, affording an excellent source of biological clarifier effluent which resembled the typical effluent from the biological pilot plant.

Referring to Figure 27, the biological clarifier effluent color averaged 0.089 FCU; the resin effluent varied between 0.001 and 0.059 FCU, depending on the volume of waste treated since resin regeneration. The cyclic nature of the process is evident from the resin effluent color variation. The percent color removals for the test period are shown in Figure 28. The average percent color removal for the entire period was 81%. A summary of the average resin effluent quality and percent reductions for all the parameters monitored during the study are given in Table 12. The resin has the capability to treat between 670 and 960 liters of waste per liter of resin before regeneration is necessary.

The results of this pilot plant confirm that resin treatment of the biological clarifier effluent is an effective method for trace color removal.

HEAVY METALS

The concentration of heavy metals in the biological sludge was observed during this study. Regular wasting of sludge was found to drastically reduce the heavy metal concentrations in the sludge, yielding copper, chromium, and zinc concentrations of 1 to 5 mg/l. Periodic sludge wasting yielded higher concentrations ranging from 25 to 70 mg/l (see Table 13). Feed concentrations were generally from 0 to 2 mg/l. Since high metal concentrations may impede normal biological growth, continual sludge wasting is most desirable.

Figure 27

Resin treatment of clarifier effluent
(FR-56 resin)

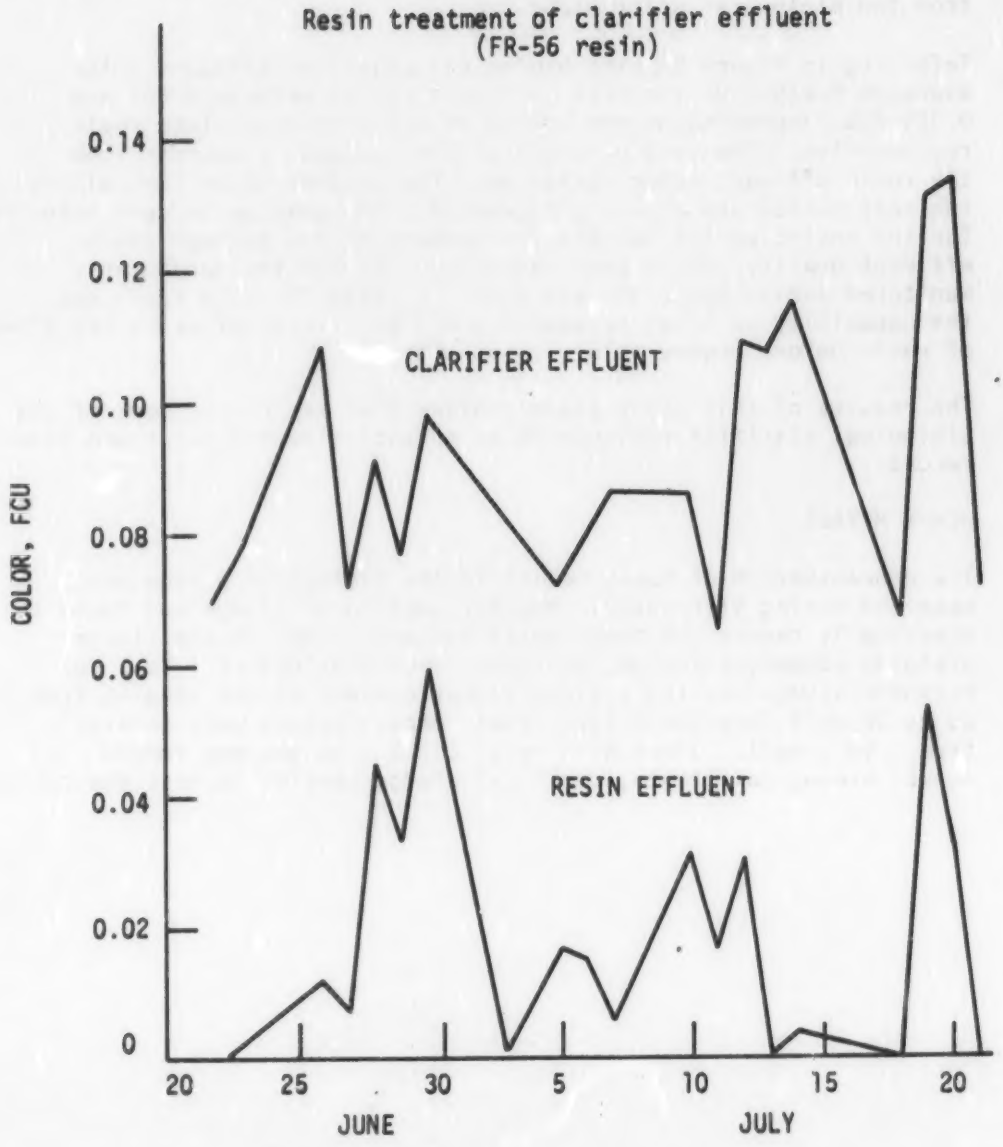


Figure 28

Pilot plant performance
(FR-56 resin)

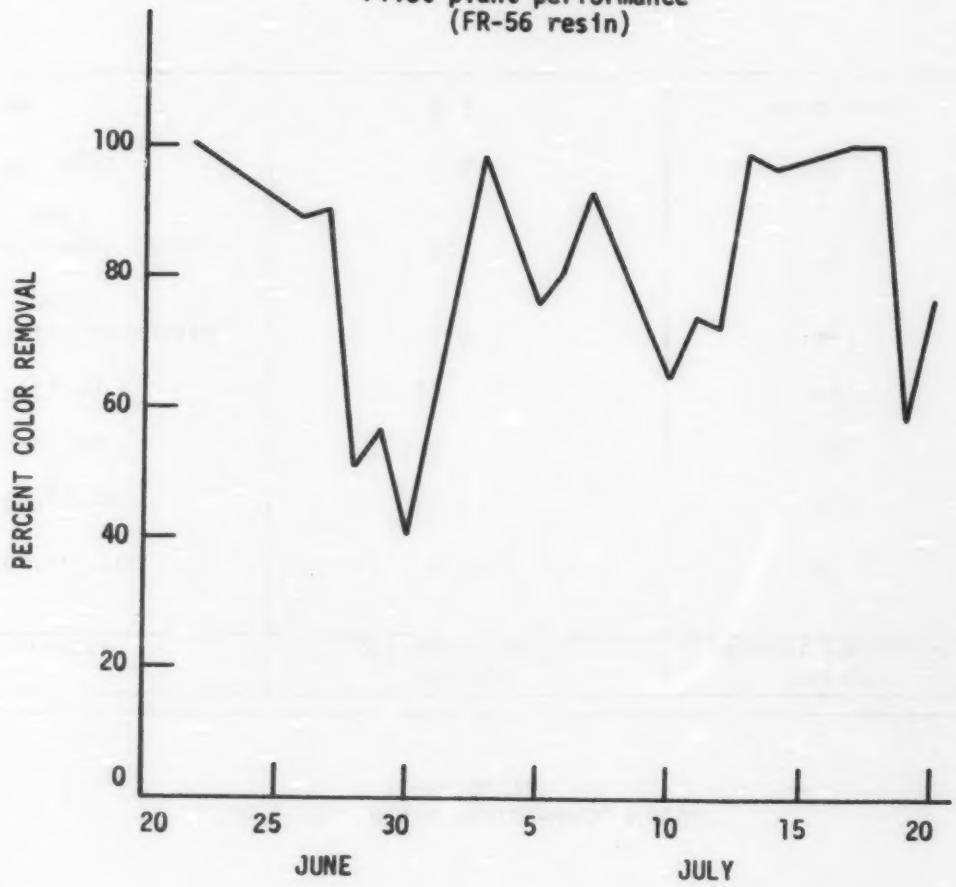


Table 12. RESIN PERFORMANCE SUMMARY
FR-56 Resin

Parameter	Average effluent quality	Average percent reduction
Color, FCU	0.022	81
BOD_5, mg/l	1.6	14
COD, mg/l	128	25
TOC, mg/l	23	26
Total phosphate, mg/l	2.0	49
Nitrogen (NH_3), mg/l	2.3	0
SS, mg/l	3.6	56
pH	8.1	No change

Table 13. HEAVY METAL CONCENTRATIONS IN RETURN BIOLOGICAL SLUDGE

Metal	Periodic wasting	Regular wasting
Copper[a], mg/l	23.8	1.0
Chromium[b], mg/l	68.6	5.2
Zinc[c], mg/l	23.8	3.7

a Typical copper influent concentration = 0.15 mg/l
b Typical chromium influent concentration = 2.2 mg/l
c Typical zinc influent concentration = 0.45 mg/l

SECTION VII

KINETIC EVALUATIONS

The biokinetic rate of oxidation of Cone Mills' waste was found to be dependent on the level of aeration within the reactors. As reported earlier, an increase in aeration in Reactor 1 resulted in an increase in BOD_5 and color removals. This increase is confirmed in Figure 29. The organic removal rate was $k_1 = 0.00217$/day for normal aeration, but increased to $k_1' = 0.00794$/day with additional aerators.

The relationship of concern here is:

$$\frac{S_1 - S_e}{X_v \quad t} = k\, S_e \qquad (2)$$

Under optimum conditions, the design equation for the first reactor would be:

$$\frac{S_1 - S_e}{X_v \quad t} = 0.00794\, S_e$$

where:

S_1 = influent BOD_5 concentration, mg/l

S_e = effluent BOD_5 concentration, mg/l

X_v = mixed liquor volatile suspended solids, mg/l

t = reactor retention time, days

The observed biokinetic rates for the second and third reactors are shown in Figures 30 and 31. As expected, these biokinetic rates are decreasing in order. Reactor 2 has a rate of 0.000689/day, while the third reactor is 0.000299/day. This is because the organic contaminants most easily degraded are biologically oxidized first (in Reactor 1), giving the highest biokinetic rate constant. The more difficult to degrade contaminants are oxidized later (in Reactor 2 and 3), yielding lower rates.

Figure 29

Biokinetic rate
reactor 1

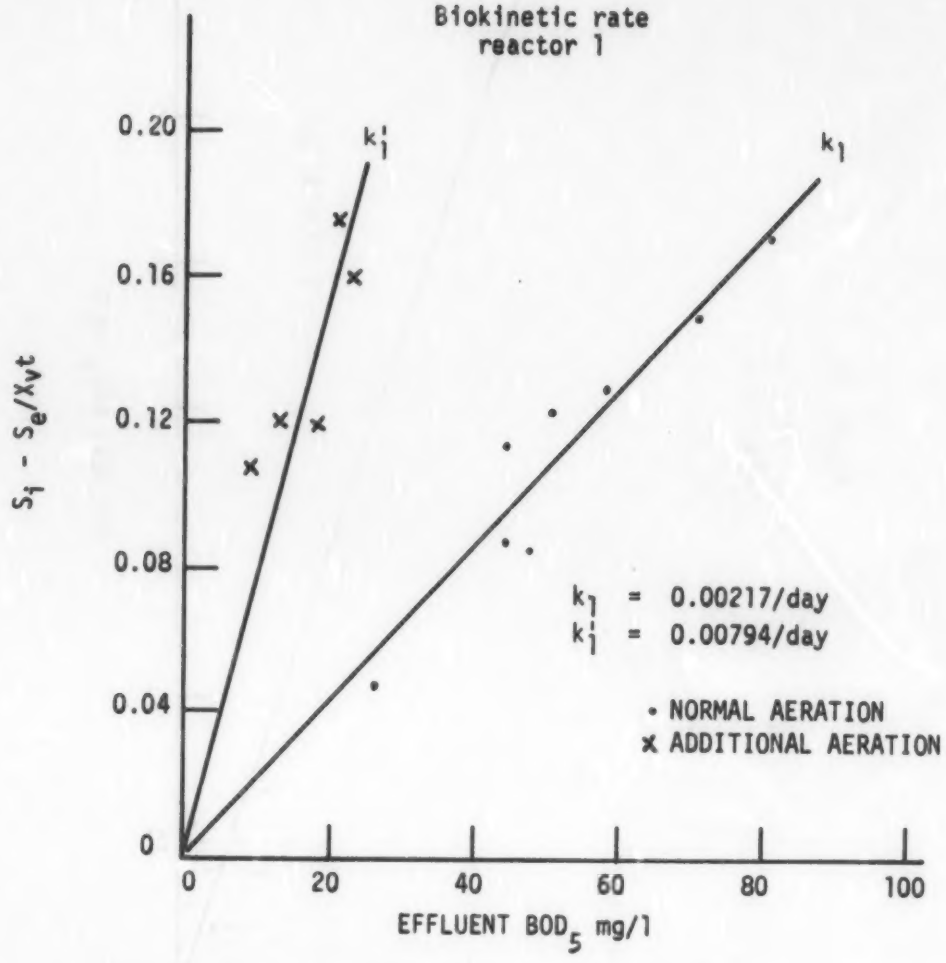


Figure 30

Biokinetic rate
reactor 2

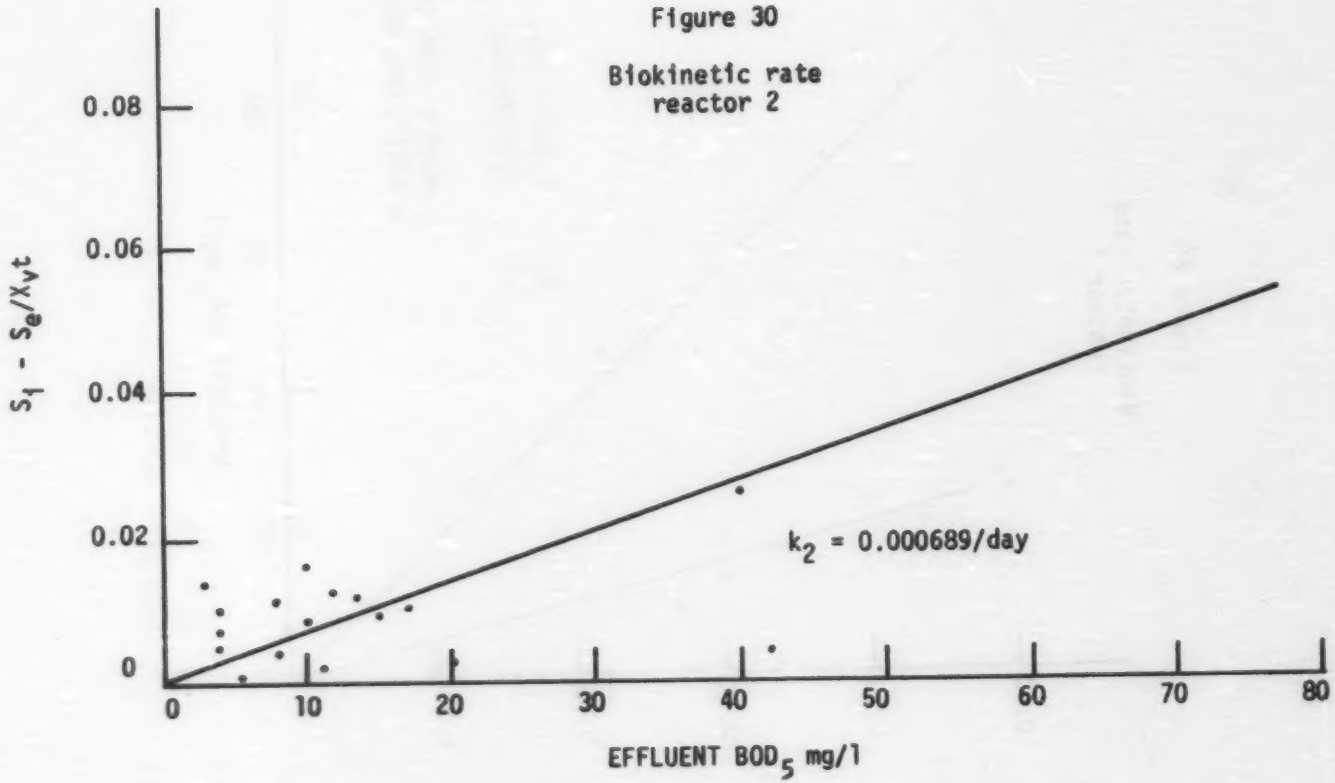
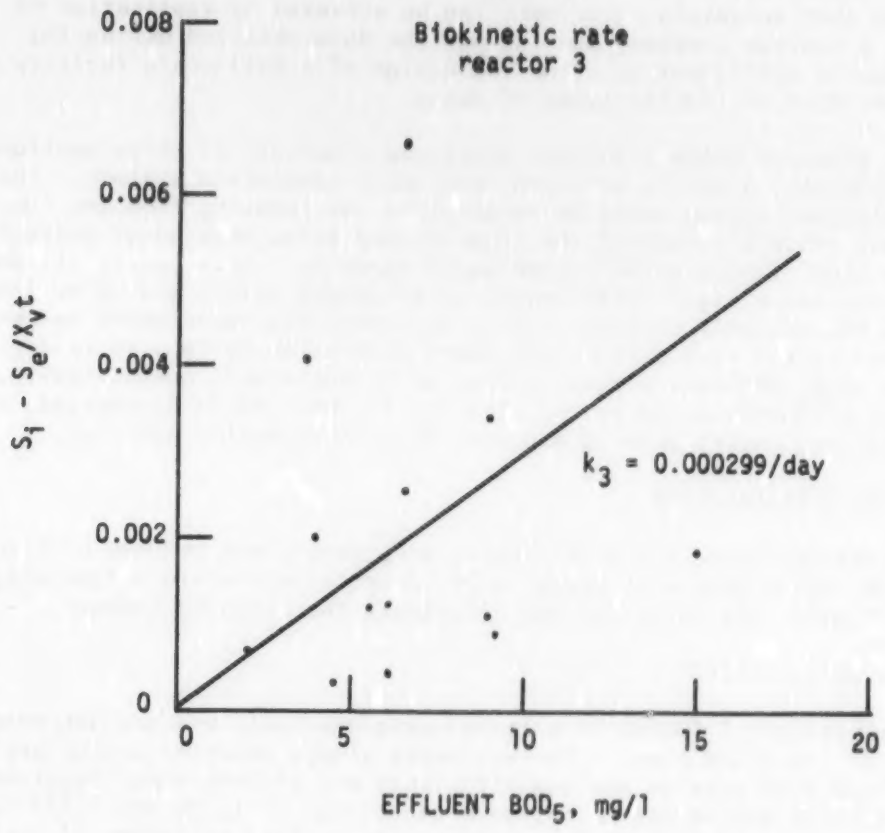


Figure 31


Biokinetic rate
reactor 3
0.008
0.006
0.004
0.002
0
$S_i - S_e/X_v t$
k_3 = 0.000299/day
0
5
10
15
20
EFFLUENT BOD_5, mg/l

SECTION VIII

FULL-SCALE MODEL

The laboratory and pilot plant investigations on Cone Mills' waste show that successful treatment can be achieved by application of the processes studied, and further the data obtained during the study is sufficient to allow the design of a full-scale facility to treat this or similar types of waste.

The proposed waste treatment plant would consist of three sections: biological, alum flocculation, and resin adsorption systems. The biological system would be responsible for removing from the raw plant waste the bulk of the organics and associated color dyestuffs. The alum flocculation system would serve to remove nearly all phosphates and a significant amount of suspended solids and color from the biologically treated waste. Any remaining color would be removed by the last system, the resin adsorption system, to render the plant effluent virtually free of objectionable contamination. Such effluents could be recycled for further use or discharged into receiving waters pending approval from governmental agencies.

PROCESS DESCRIPTION

A detailed description of a waste treatment plant capable of treating 3,785 cubic meters of waste daily is presented herein. Flow diagrams in Figures 32a, 32b, and 32c illustrate the proposed process.

BIOLOGICAL SYSTEM

The biological system is a carbon catalyzed unit process patterned after the pilot plant. Two activated sludge aeration basins are utilized to provide maximum efficiency and minimum space requirements. The first and second basins have capacities of 2,195 and 1,173 cubic meters, respectively. Each basin contains five kilograms of activated carbon per cubic meter.

Raw waste enters the first basin where it is combined with return activated sludge and colored spent regenerate from the resin adsorption system. After 14 hours aeration, the partially treated waste proceeds to the second aeration basin where further degradation occurs. After approximately 7.4 hours retention period, the biologically treated waste is clarified in a 155 square meter clarifier. The separated activated sludge is returned to the first basin, except for a purge stream which is filtered on a 1.9 square meter vacuum filter.

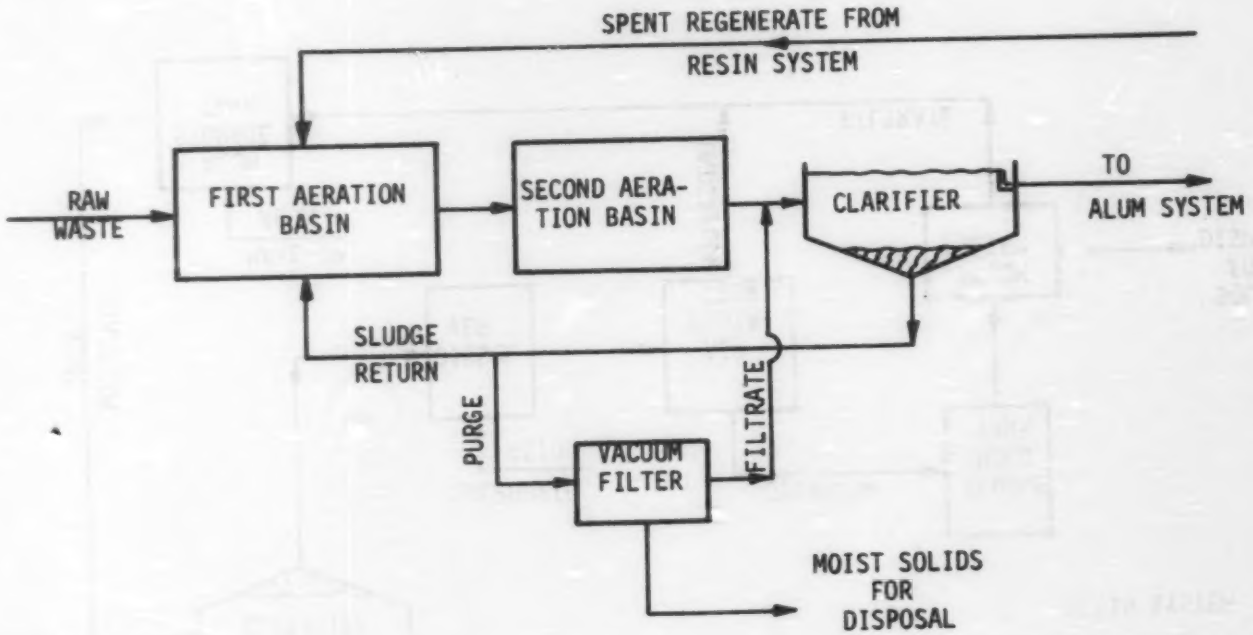


Figure 32a

Biological system

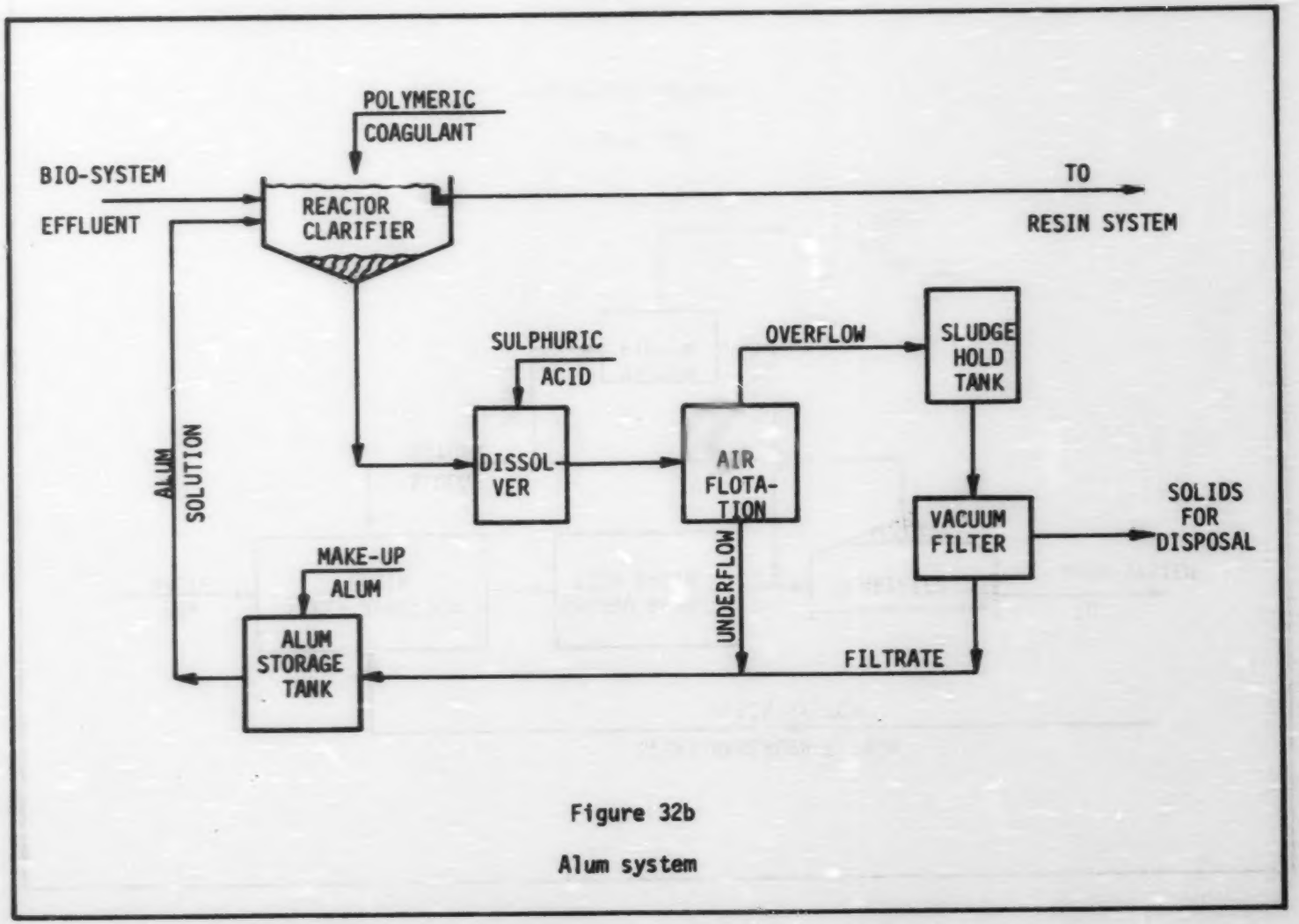


Figure 32b

Alum system

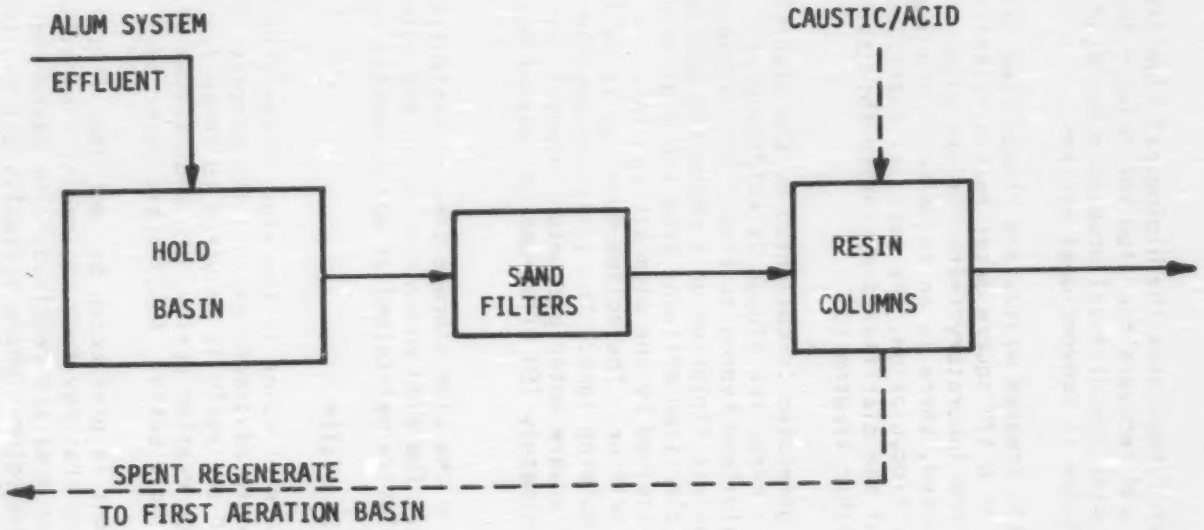


Figure 32c

Resin adsorption system

The clarifier effluent proceeds to the alum system for further treatment.

ALUM SYSTEM

The alum system flocculates the biological clarifier effluent by alum addition and recovers the alum for reuse. The alum recovery process alleviates the disposal problem associated with the voluminous alum sludge in conventional systems.

The biologically treated wastes are flocculated with 300 mg/l alum in the center of a 177 square meter reactor-clarifier for a 10 minute period. From laboratory tests, it was noted that when a polymeric coagulant is added, there is an increase in the size of the floc formed. After flocculation, the waste is clarified in the outermost portion of the clarifier and sent to the resin adsorption system for further treatment.

The alum floc generated is collected by the clarifier and pumped to a mixing tank. Here, the sludge is acidified with sulphuric acid to dissolve the aluminum hydroxide floc. The recovered alum solution passes on to an air flotation unit where the undissolved solids are removed. The clarified effluent from the 0.93 square meter flotation unit is received by the alum storage tank for eventual feed to the reactor-clarifier. The solids overflow is collected continuously in the sludge holding tank. The collected overflow is filtered daily on a 2.8 square meter precoated rotary filter during an 8-hour period. Approximately 159 kilograms per day of moist solids will be collected.

Alum is added to the alum storage tank to replenish alum losses in the process. The alum concentration in the solution fed to the reactor-clarifier is maintained at approximately 2.5%.

RESIN ADSORPTION SYSTEM

The trace amounts of color in the alum system effluent are removed by adsorption onto adsorbent resin. The process is cyclic in nature; regeneration of the resin is required to renew its adsorptive capacity During this regeneration period, the alum system effluent must be contained in a hold basin. A 379 cubic meter basin is provided.

The alum effluent is pretreated by four sand filter beds to remove suspended solids that may foul the resin. Approximately 13 square meters of filter area are required. The waste then passes to the resin adsorption columns where virtually all the trace color is removed from the stream, rendering a plant effluent suitable for discharge or potential reuse.

The adsorptive resin is housed in three columns piped in parallel and charged with 18.4 cubic meters of resin. Each column is equipped with a resin support media and distributors above and below the resin bed for distribution of waste and regenerate solutions.

Regeneration of the resin column is determined by the effluent color, or by a timer. During regeneration, the waste flow is stopped for the duration and allowed to collect in the hold basin. A warm 2% solution of caustic is passed downward through the columns, followed by a rinse of warm water. The columns are then neutralized with a cold 2% solution of sulphuric acid and given a final water rinse. The regenerate streams contain the color and organics stripped from the resin. These are recycled to the first biological aeration basin for eventual degradation. Their total volume is approximately 1% of the volume of waste treated.

PROJECTED EFFLUENT QUALITY

The model waste treatment plant is expected to provide a high level of treatment which will render the waste suitable for discharge or reuse.

The projected effluent qualities from the individual treatment systems are shown in Table 14. Using the average Cone Mills' waste characteristics, the model plant is expected to provide virtually complete removal of BOD_5 and color (over 98% each), while COD, suspended solids, and phosphate removals were approximately 95%. Nitrogen (as ammonia) removal would be lower, approximately 75%.

ECONOMICS

The model waste treatment plant utilizes several processes that reduce the capital and operating costs. First of all, the use of staged aeration and carbon catalysis in the biological system allows smaller basin sizes than required in conventional treatment. Secondly, the use of alum regeneration in the alum system gives savings in operating expense. Chemical and sludge disposal costs are reduced significantly.

A summary of the estimated capital expenditure for a 3,785 m^3/day model treatment plant employing the three treatment systems is given in Table 15. The total capital expenditure is estimated to be $1.49 million.

OPERATING COSTS

The total chemical, utilities, and labor costs to operate the entire proposed plant are shown in Table 16.

Table 14. PROJECTED EFFLUENT QUALITY

Parameter	Raw waste	Treatment step			Overall percent reduction
		Biological	Alum	Resin	
BOD_5, mg/l	465	5	3.1	2.7	99+
COD, mg/l	1415	127	103	77	95
SS, mg/l	157	27	34	10	94
Nitrogen, mg/l	10.5	2.5	2.5	2.5	75
Phosphate, mg/l	1.8	1.8	0.1	0.1	95+
Color, FCU	1.217	0.122	0.095	0.020	98+
pH	12 - 13	7.5 - 8.0	7.5	7.5	-

Table 15. ESTIMATED CAPITAL COST
1972 base

System	Installed cost, $
Biological system	
Activated sludge basins and aerators (reinforced concrete)	
2195 cubic meter capacity	400,500
1173 cubic meter capacity	221,000
Final clarifier	168,000
Vacuum filter	42,000
Carbon	23,000
	$854,500
Alum system	
Reactor-clarifier	173,500
Flotation equipment	29,300
Tanks & feeders	34,800
Vacuum filter	48,400
Pumps	18,500
	$304,500
Resin system	
Adsorption columns, 3	80,000
Sand filters	80,000
Hold basin	29,000
Adsorbent resin	47,500
	$236,500
TOTAL INSTALLED COST[a]	$1,490,000

[a] Including contingencies, land and contractor fees

Table 16. ESTIMATED OPERATING COST
1972 Base

Material or Service	Cost, ¢
Chemicals	
Make-up carbon	2.0¢
Make-up alum	1.3¢
Sulphuric acid	5.6¢
Caustic	1.6¢
Miscellaneous	1.1¢
Utilities	2.0¢
Labor	
36 hrs/day @ $4.00/hr	14.4¢
TOTAL OPERATING COST	28.0¢[a]

[a] Per 3.79 cubic meters (1000 gallons) treated

Under the existing Federal Income Tax Laws, waste treatment facilities may be depreciated over a five year period. For purposes of this example, depreciation and capital recovery will be assumed to occur over a five-year period with an interest rate of 9%. Table 17 shows the predicted annual cost for the first five years of operation.

Table 17. ANNUAL COSTS

Cost	$
Annual operating cost	
(m^3/day treated) ($/cubic meter) (days/year)	
(3790) (0.28/3.79) (365) =	102,200
Annual depreciation	
Total installed cost/n where n = years of depreciation	
1, 490,000/5 =	298,000
Annual interest	
(principal) (interest rate) (n + 1/n)	
(1,490,000) (0.09) (6/10) =	80,460
TOTAL ANNUAL COST	480,660[a]

[a] This is equivalent to $1.32 per 3.79 cubic meters (1000 gallons) treated, and is only valid for the first five years of operation. After that period, the plant will be fully depreciated and the operating cost will drop to $0.28 per 3.79 cubic meters (1000 gallons) treated.

SECTION IX

REFERENCES

1. Eckenfelder, W. W. Water Quality Engineering for Practicing Engineers. New York, Barnes and Noble, Inc., 1970. p. 160 - 163.

2. Holman, J. P. Experimental Methods for Engineers. New York, McGraw-Hill Book Company, 1966. p. 53.

SECTION X

GLOSSARY

BOD_5 - Abbreviation for Biochemical Oxygen Demand, five day. The amount of dissolved oxygen consumed in five days by biological processes breaking down organic matter in an effluent.

COD - Abbreviation for Chemical Oxygen Demand. A measure of the amount of oxygen required to oxidize organic and oxidizable inorganic compounds in water.

Darco - Trademark for activated carbon derived from lignite and sold by ICI America, Inc., Wilmington, Delaware.

D. O.- Abbreviation for Dissolved Oxygen. The oxygen dissolved in water or sewage.

FCU - Abbreviation for Fram Color Unit. It is measured by using a variable grating spectrophotometer, where the light absorbance is measured at three wavelengths - 350, 450, and 550 millimicrons. If the light absorbance is greater than the instrument scale, the sample is diluted and a dilution multiplier is used to calculate the absorbance. The Fram Color Unit (FCU) is the sum of the corrected light absorbance at these three wavelengths.

FR-37 - Designation for synthetic resinous adsorbent sold by Fram Corporation, Providence, Rhode Island.

FR-42 - Designation for synthetic macroreticular, weak base anion exchange resin sold by Fram Corporation, Providence, Rhode Island.

FR-56 - Designation for synthetic, macroreticular, weak base, anion exchange resin sold by Fram Corporation, Providence, Rhode Island.

mg/l - Abbreviation for milligram per liter.

ml - Abbreviation for millliliter.

m^3/day - Abbreviation for cubic meters per day.

Norit II - Trademark for activated carbon derived from peat and sold by American Norit Co., Inc., Jacksonville, Florida.

Nuchar WV-G - Trademark for activated carbon derived from bituminous coal and sold by Westvaco, Covington, Virginia.

ppm - Abbreviation for parts per million. On an equal weight basis, this term can be used as an equivalent for mg/l.

TOC - Abbreviation for Total Organic Carbon. A measure of the amount of carbon in a water sample attributable to organic matter.

TOD - Abbreviation for Total Oxygen Demand. The amount of oxygen that would be consumed if a chemical were to be oxidized to the highest oxidation state of each element in the compound.